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Prepared as part of the chemistry section of the
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Energy in Chemical Reactions

J. P. Doherty
Newcastle College of Advanced Education

Gage Educational Publishing Limited

The Jacaranda Press

©Gage Educational Publishing Limited 1975
164 Commander Blvd., Agincourt, Ontario

©Jacaranda Press Pty Ltd 1972

First published 1972 by
JACARANDA PRESS PTY LTD
65 Park Road, Milton,
Queensland, Australia

PRINTED AND BOUND IN Canada
ISBN 7715-7401-0

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H 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.8	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 39.9
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.8	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.5	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** (99)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57-71 **La-Lu**	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Ti** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (210)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89-103 **Ac-Lw**	104	105													

57 **La** 138.9	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	**Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
89 **Ac** (227)	90 **Th** 232.0	91 **Pa** (231)	92 **U** 238.0	93 **Np** (237)	94 **Pu** (242)	95 **Am** (243)	96 **Cm** (248)	97 **Bk** (247)	98 **Cf** (249)	99 **Es** (254)	100 **Fm** (253)	101 **Md** (256)	102 **No** (254)	103 **Lw** (257)

Parenthetical values are mass numbers of the isotopes with longest half lives

INTERNATIONAL ATOMIC WEIGHTS
(*Atomic Weights relative to* $^{12}C = 12$ *exactly*)

Atomic Number	*Name*	*Symbol*	*Atomic Weight*	*Atomic Number*	*Name*	*Symbol*	*Atomic Weight*
1	Hydrogen	H	1.008	31	Gallium	Ga	69.72
2	Helium	He	4.003	32	Germanium	Ge	72.59
3	Lithium	Li	6.939	33	Arsenic	As	74.92
4	Beryllium	Be	9.012	34	Selenium	Se	78.96
5	Boron	B	10.81	35	Bromine	Br	79.91
6	Carbon	C	12.01	36	Krypton	Kr	83.80
7	Nitrogen	N	14.01	37	Rubidium	Rb	85.47
8	Oxygen	O	16.00	38	Strontium	Sr	87.62
9	Fluorine	F	19.00	39	Yttrium	Y	88.91
10	Neon	Ne	20.18	40	Zirconium	Zr	91.22
11	Sodium	Na	22.99	41	Niobium	Nb	92.91
12	Magnesium	Mg	24.31	42	Molybdenum	Mo	95.94
13	Aluminium	Al	26.98	43	Technetium*	Tc	(99)
14	Silicon	Si	28.09	44	Ruthenium	Ru	101.1
15	Phosphorus	P	30.97	45	Rhodium	Rh	102.9
16	Sulphur	S	32.06	46	Palladium	Pd	106.4
17	Chlorine	Cl	35.45	47	Silver	Ag	107.9
18	Argon	Ar	39.95	48	Cadmium	Cd	112.4
19	Potassium	K	39.10	49	Indium	In	114.8
20	Calcium	Ca	40.08	50	Tin	Sn	118.7
21	Scandium	Sc	44.96	51	Antimony	Sb	121.8
22	Titanium	Ti	47.90	52	Tellurium	Te	127.6
23	Vanadium	V	50.94	53	Iodine	I	126.9
24	Chromium	Cr	52.00	54	Xenon	Xe	131.3
25	Manganese	Mn	54.94	55	Caesium	Cs	132.9
26	Iron	Fe	55.85	56	Barium	Ba	137.3
27	Cobalt	Co	58.93	57	Lanthanum	La	138.9
28	Nickel	Ni	58.71	58	Cerium	Ce	140.1
29	Copper	Cu	63.54	59	Praseodymium	Pr	140.9
30	Zinc	Zn	65.37	60	Neodymium	Nd	144.2

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

INTERNATIONAL ATOMIC WEIGHTS

(Atomic Weights relative to ^{12}C = 12 exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
61	Promethium*	Pm	(145)	86	Radon*	Rn	(222)
62	Samarium	Sm	150.4	87	Francium*	Fr	(223)
63	Europium	Eu	152.0	88	Radium*	Ra	(226)
64	Gadolinium	Gd	157.3	89	Actinium*	Ac	(227)
65	Terbium	Tb	158.9	90	Thorium*	Th	232.0
66	Dysprosium	Dy	162.5	91	Protactinium*	Pa	(231)
67	Holmium	Ho	164.9	92	Uranium*	U	238.0
68	Erbium	Er	167.3	93	Neptunium*	Np	(237)
69	Thulium	Tm	168.9	94	Plutonium*	Pu	(242)
70	Ytterbium	Yb	173.0	95	Americium*	Am	(243)
71	Lutetium	Lu	175.0	96	Curium*	Cm	(248)
72	Hafnium	Hf	178.5	97	Berkelium*	Bk	(247)
73	Tantalum	Ta	180.9	98	Californium*	Cf	(249)
74	Tungsten	W	183.9	99	Einsteinium*	Es	(254)
75	Rhenium	Re	186.2	100	Fermium*	Fm	(253)
76	Osmium	Os	190.2	101	Mendelevium*	Md	(256)
77	Iridium	Ir	192.2	102	Nobelium*	No	(254)
78	Platinum	Pt	195.1	103	Lawrencium*	Lw	(257)
79	Gold	Au	197.0	104	(Kurchatovium)		
80	Mercury	Hg	200.6				
81	Thallium	Tl	204.4				
82	Lead	Pb	207.2				
83	Bismuth	Bi	209.0				
84	Polonium*	Po	(210)				
85	Astatine*	At	(210)				

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

Preface

In this booklet, the topic of chemical energy has been approached in the following way:

- Firstly, it is considered against a broad background of the history of man, the development of chemistry and energy changes generally.
- Then, in each section an aspect or aspects of chemical energy have been presented as simply and as clearly as possible; these fundamental points have been developed further by means of questions and answers.
- Finally, nuclear energy and its relationship to chemical energy have been considered, both from the scientific and social point of view.

After completing this unit you should have some understanding of:

- the relation between social change and the growth of science;
- the importance of chemical energy to man and to the development of chemistry;
- the relationship of chemical energy to other forms of energy;
- how changes in chemical energy are measured, interpreted and used;
- the application of the First and Second Laws of Thermodynamics to chemistry;
- the 'driving forces' of chemical reactions; and
- the similarities and differences between chemical and nuclear energy.

You should be able to:

- interpret and write thermochemical equations;
- interpret and draw enthalpy diagrams;
- calculate heats of reaction from appropriate data;
- calculate and use standard enthalpies of formation;
- calculate and use bond energies;
- calculate the mass changes associated with energy changes; and
- predict the feasibility of an untried chemical reaction under given conditions.

Is Chemical Energy Important?

On July 16 1969, television screens around the world showed the terrific blast of energy which slowly lifted the 2768 tonne Apollo 11 from its launching pad and sent it hurtling towards the moon. It seems a far cry from that spectacle to that of prehistoric men huddled for warmth and protection around their small cave fire. Despite the obvious contrast, these two events have some features in common. They both mark major advances by our species *Homo sapiens*, and they both depend upon the release of energy from a chemical reaction—the combustion of kerosene for the moon rocket and of wood for the prehistoric men.

The significance of man's first landing on the moon has been adequately discussed in many newspaper and magazine articles; the importance of man's first use of energy from a fire is often overlooked. Fire was man's first addition to his own natural energy. Other animals are restricted still to the energy released by the oxidation of food within their bodies, i.e. the energy released by respiration.

In the history of man's endeavour to control his environment, the mastery of fire ranks in importance alongside the development of agriculture and the scientific revolution. As his knowledge and skill in using the power of combustion increased, he burnt ever increasing quantities of fuel and thereby achieved remarkable mastery over both the inanimate and living environment. The current concern about conservation and pollution indicates that man has not always used this control wisely and it is possible that he may eventually destroy himself; nevertheless, the energy from fire is the basis both for man's achievements and for his current problems.

Chemical Changes which Absorb Heat

Quite early in his history, man found that the energy released by the chemical reactions of a fire could be used to produce other chemical changes. The heat could be used to change substances into different and more useful substances, e.g. to cook food, making it more digestible and more palatable; to change clay into pottery; to smelt ores, producing metals; to make glass.

Such changes which require the absorption of heat are called **endothermic.** Combustion and other changes which liberate heat are called **exothermic.** Man's social life was changed significantly by these useful endothermic changes which he brought about by the use of fire. The impact of the production of metals was so marked, that the history of man is often divided into the Stone Age, the Bronze Age and the Iron Age.

Mechanical Energy and Chemical Change

A later cause of major social change was the discovery that the heat from a chemical change could be used to produce mechanical energy, i.e. to cause the movement of objects. One of the first chemical changes to be used for this purpose was the explosion of gunpowder. This explosion—like most explosions—is characterized by the *formation of gases* and the release of heat energy in a *very short interval of time*. Because of the released heat energy the gases expand very quickly, and thus could be used to speed a cannon ball or blast a rock from a quarry. The introduction of gunpowder into Europe—and indeed into other areas—altered the existing relationships between classes and nations, because it made obsolete the existing methods of defence, e.g. castles.

Later still, the Industrial Revolution (which vastly increased the use of machines to do man's work) started with the discovery of the steam engine, in which the energy from the combustion of coal or other fuel is converted into mechanical energy. During the last one hundred years, the internal combustion engine, such as we have in the petrol engine, has been used increasingly to make available the chemical energy stored in petroleum. Now, in the space age, we have the jet engine and the rocket to release tremendous power from a variety of fuels.

At the present time, although it is true that man does derive energy from sources other than chemical ones, the combustion of various fuels still provides the greatest part of the vast quantities of energy that are used. In Australia, for example, well over ninety per cent of commercial and domestic power is derived from the combustion of coal, coal gas, petroleum and natural gas.

Electricity and Chemical Change

One other device, which because of its theoretical and practical importance must not be forgotten, is the voltaic cell or battery in which the energy from a chemical change is converted directly to electrical energy. The discovery of the voltaic cell by Alessandro Volta led quickly and directly to the realization that the reverse action was also possible. Electricity from the voltaic cell or battery could be used to supply the energy for numerous endothermic reactions—the process of electrolysis. Modern industries in which electricity is used; e.g. to refine copper, to extract magnesium from the sea, to produce chlorine from salt, to protect and adorn metals by electroplating; bear witness to the considerable practical importance of the use of electrical energy to bring about chemical changes.

Light and Chemical Change

It is of interest to note that while energy is usually released from chemical reactions as heat, and less frequently as mechanical or electrical energy, in some few reactions it is released directly as light. The cold light of certain living organisms, e.g. the fire-flies,

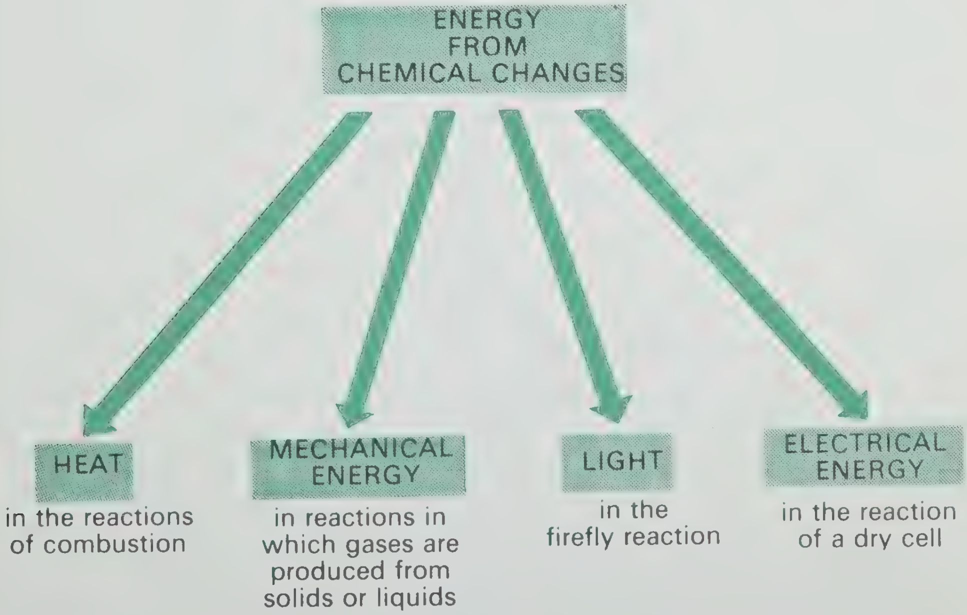

ENERGY FROM CHEMICAL CHANGES
HEAT
in the reactions of combustion
MECHANICAL ENERGY
in reactions in which gases are produced from solids or liquids
LIGHT
in the firefly reaction
ELECTRICAL ENERGY
in the reaction of a dry cell

Figure 1. Forms of energy which can be obtained directly from chemical reactions

is produced when a protein derivative luciferin, is oxidized by atmospheric oxygen. A second example is the light that is produced when phosphorus or its trioxide is oxidized by air.

These reactions in which light is emitted are not of very great theoretical or practical importance. On the other hand, the reactions which proceed by the absorption of light energy are more numerous and include what is probably the most important of all chemical reactions, i.e. the reaction of photosynthesis.

$$\begin{matrix}\text{carbon}\\ \text{dioxide}\end{matrix} + \text{water} + \begin{matrix}\text{light}\\ \text{energy}\end{matrix} \xrightarrow{\text{chlorophyll}} \text{carbohydrate} + \text{oxygen}$$

It is by this reaction that the energy of the sun is stored as chemical energy of the plant. This store of energy is used directly by the plant for its life processes; indirectly by other living organisms; and by man as the source (in the form of wood, coal and petroleum) of most of his energy.

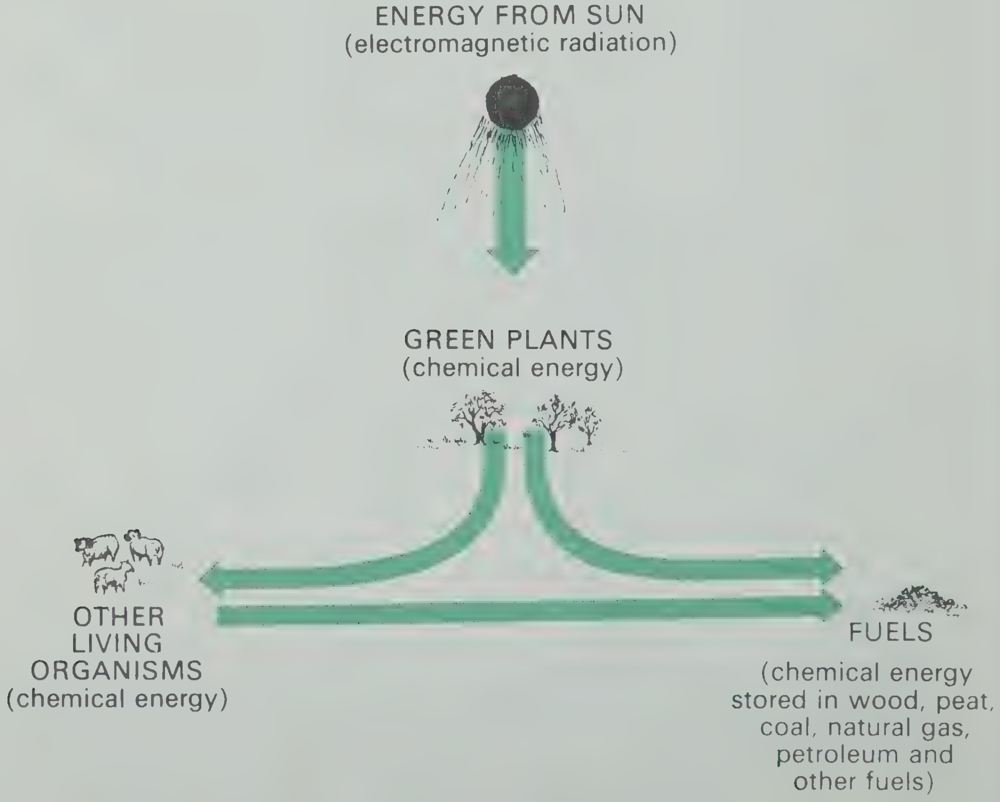

ENERGY FROM SUN
(electromagnetic radiation)
GREEN PLANTS
(chemical energy)
OTHER LIVING ORGANISMS
(chemical energy)
FUELS
(chemical energy stored in wood, peat, coal, natural gas, petroleum and other fuels)

Figure 2. Energy from the sun is stored as chemical energy, firstly by plants and hence in other organisms. By these means it accumulates in the substances man uses as fuels.

Exoergic and Endoergic Changes

Because chemical changes can give out and absorb energy in forms other than heat, in this booklet the traditional terms of **exothermic** and **endothermic** will be discarded in favour of the wider and more general terms of exoergic and endoergic.

An exoergic change is one in which energy is emitted.

An endoergic change is one in which energy is absorbed.

Theoretically, there is the possibility of a chemical change in which energy is not absorbed or emitted. Such a change is known as **nulloergic.** If this change does occur, it is certainly very rare. Some changes which were thought to be within this class have been shown by more accurate measurement to be either slightly exoergic or endoergic.

Exercises

1 Five changes are listed below. Consider each change and state whether it is
  (a) physical or chemical
  (b) exoergic or endoergic.
    (i) sublimation of dry ice,
    (ii) combustion of petrol,
    (iii) electrolysis of water,
    (iv) charging of a car battery,
    (v) formation of hail from rain.

2 carbon + oxygen $\longrightarrow$ carbon dioxide + heat

iodine$_{(s)}$ + heat $\longrightarrow$ iodine$_{(g)}$

Equations like the above in which the emission or absorption of energy is indicated, are called **thermochemical equations.** Write the appropriate thermochemical equations for the following:
  (i) combustion of sulphur,
  (ii) the process of respiration (oxidation of glucose),
  (iii) evaporation of water,
  (iv) solidification of lava,
  (v) formation of snow from water vapour.

3 If man had not discovered fire, is there any other chemical reaction that could have served the same social purposes that fire has served?

Chemistry and Chemical Energy

From the Stone Age to the Space Age, fire has supplied the ever-increasing quantities of energy that man has required for his widespread activities. In chemistry too, fire has played an essential part. Chemistry has its roots in the arts and crafts of the ancient civilizations and most of these depended upon the energy derived from fire. The Greek philosophers found 'fire' so basic to the nature of things that they considered it to be one of the fundamental elements of the universe. During the Middle Ages, the alchemists made fire the main instrument in their persistent endeavours to change base metals into gold. Antoine Lavoisier's investigation of the theory of combustion during the latter part of the eighteenth century is regarded as one of the foundation stones of modern chemistry.

In these and other ways, the energy derived from fire has directly stimulated and guided the development of chemistry. However, one very important effect on chemistry was an indirect one. The increasing use of the steam engine as a source of mechanical energy in the early nineteenth century stimulated the brilliant

Figure 3. Sadi Carnot (1796-1832), engineer in the French army, was the son of one of Napoleon's military leaders. His paper 'Reflections on the Motive Power of Fire . . .' laid the foundation for a whole field of thought, the field of thermodynamics. Sadi—the name was derived from that of a medieval Persian poet who was popular at this time—was a reserved, almost taciturn, man with a hatred of any form of publicity; he was passionately fond of music and an excellent violinist. He never married and he died of cholera at the age of 36.

young French engineer, Sadi Carnot, to try to improve the efficiency of the steam engine. His careful studies of the principles underlying the change of energy from heat energy to mechanical energy, and mechanical energy to heat energy, led to the development of the science of **thermodynamics.**

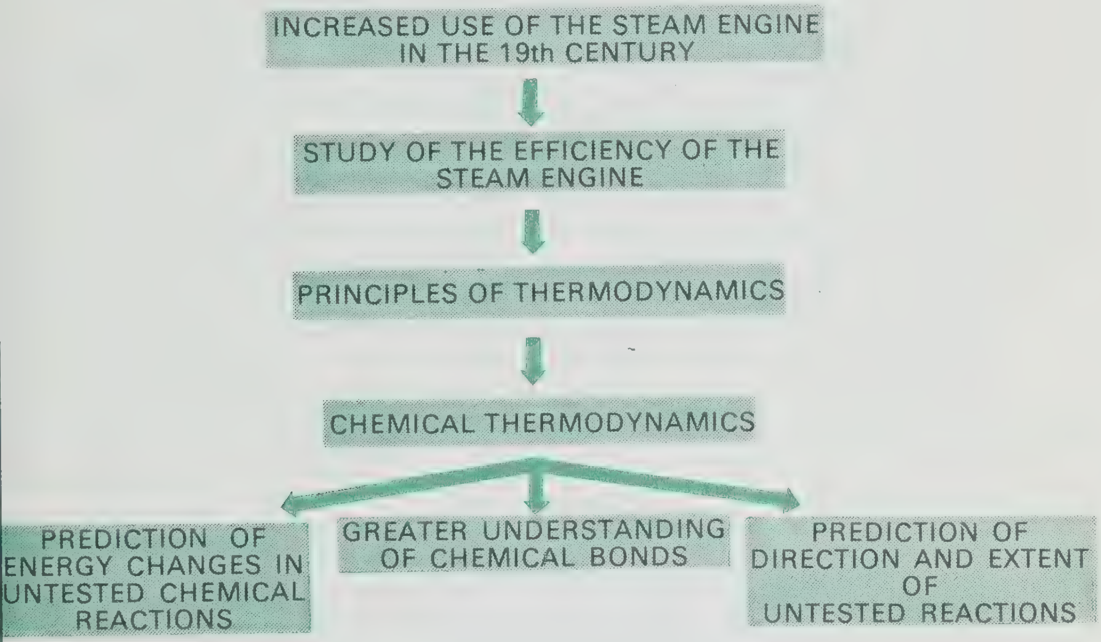

INCREASED USE OF THE STEAM ENGINE IN THE 19th CENTURY
STUDY OF THE EFFICIENCY OF THE STEAM ENGINE
PRINCIPLES OF THERMODYNAMICS
CHEMICAL THERMODYNAMICS
PREDICTION OF ENERGY CHANGES IN UNTESTED CHEMICAL REACTIONS
GREATER UNDERSTANDING OF CHEMICAL BONDS
PREDICTION OF DIRECTION AND EXTENT OF UNTESTED REACTIONS

Figure 4. The reaction between social change and the theory of chemical energy

When the principles of thermodynamics were applied to the energy changes associated with chemical reactions, it became possible to:

- predict the *energy changes* associated with as yet untested chemical changes;
- obtain a better understanding of the *strength* and *nature* of the bonds between atoms in chemical combination; and
- predict the *direction* and *extent* to which untried chemical reactions will proceed.

Here is the result of innovation in an area not directly related to chemistry. A social development (the increased use of steam power) triggered a scientific study in the field of physics, and indirectly had a profound effect on the study of chemical reactions.

Discussion

1. 'Fire is a great teacher, man's greatest master in the art of chemistry.' What justification is there for this statement?

By means of fire man has learnt how to:

- speed up chemical reactions of all kinds;
- bring about important endoergic reactions;
- develop the industries based on these reactions
  e.g. smelting of metallic ores,
  production of coke, tar and gas from coal,
  cracking of petroleum fractions;
- purify substances by such means as distillation, evaporation, sublimation, etc.;
- distinguish substances by such means as melting points, boiling points, flame tests, charcoal block tests;
- increase his understanding of chemical reactions and chemical bonds.

2. Did any other form of chemical energy, apart from that released by fire, play an important part in the development of chemistry?

The introduction of the voltaic cell at the start of the nineteenth century had a very great effect on both the practical and teoretical aspects of chemistry.

Practically, it provided the chemist with a new means of decomposition—**electrolysis**. This enabled him to decompose substances which had resisted other means of disintegration, and thereby to isolate a number of new elements.

Theoretically, it led to the study of **electrochemistry**, and to the development of such important theories as those of **ionization** and **electrode potentials**. More importantly, the decomposition of substances by electrolysis suggested that the basis of the chemical bond was electrostatic attraction.

3. The introduction of the steam engine into society ultimately stimulated and guided the study of chemical thermodynamics. Can you give any other examples of social changes guiding the direction and development of chemistry?

Many social developments have had their impact on chemistry, but their results have not been as clear-cut as the influence of the steam engine.

In the early part of the nineteenth century the use of coal gas as an illuminant became popular. With the increased production of coal gas, the accumulation of the by-product coal tar, became a nuisance. Eventually this led to the investigation of the substances that could be extracted or derived from it. The variety and value of the substances —dyes, drugs, explosives, perfumes and plastics—obtained from coal tar stimulated and directed the growth of organic chemistry for half a century.

The Measurement of Chemical Energy

For thousands of years artisans, craftsmen, natural philosophers and alchemists had understood that some chemical changes liberate heat, whilst others require heat for the change to occur.

A deeper understanding of the relationship between energy and chemical change became possible when the energy emitted or absorbed was measured. It is only within the last two hundred years that this task has been undertaken. One of the first attempts was that of Antoine Lavoisier (1743-94) and Pierre Laplace (1749-1827), in the period from 1782 to 1784.

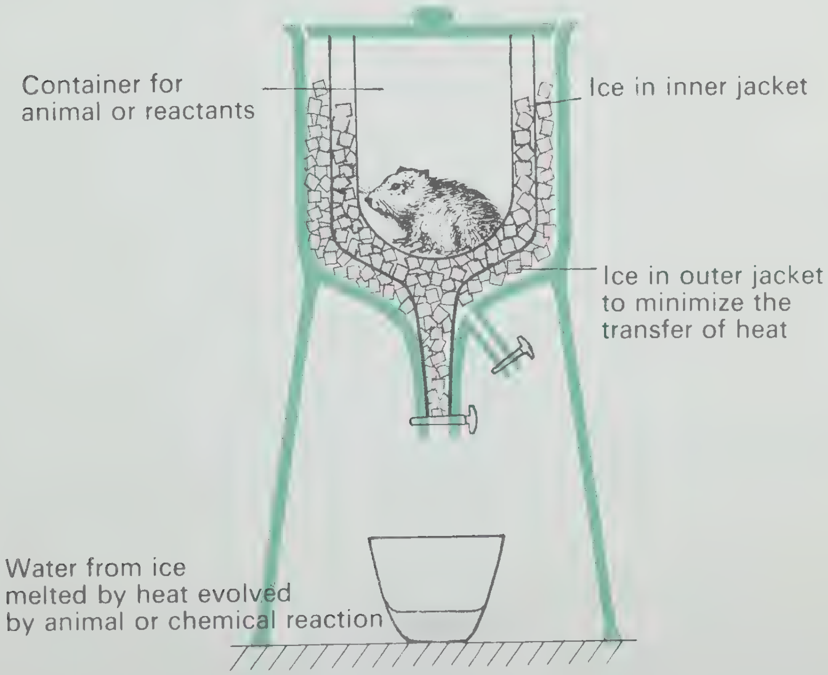

Container for animal or reactants
Ice in inner jacket
Ice in outer jacket to minimize the transfer of heat
Water from ice melted by heat evolved by animal or chemical reaction

Figure 5. Ice calorimeter of Lavoisier and Laplace 1780

They used a **calorimeter**, based on one that had been devised earlier in the same century by a Scottish chemist, Joseph Black. In this instrument, the quantity of heat given out was measured by the weight of ice melted. Lavoisier and Laplace investigated the heat given out in a variety of chemical reactions. They also used the calorimeter to study the process of animal respiration.

A guinea-pig was placed in the calorimeter for ten hours. The heat given out by the respiration of its body cells melted some ice; the resulting water was collected and found to weigh thirteen ounces. The weight of carbon dioxide given out by the guinea-pig during the ten hours was also determined. The weight of carbon which must be burnt to produce the same weight of carbon dioxide was found by experiment. This weight of carbon was then burnt in the calorimeter and it was found that the heat evolved melted 10.5 ounces of ice. Taking into account the inevitable errors in the experiment, Lavoisier and Laplace concluded that respiration was essentially the same process as the slow combustion of carbon.

Exercises

4 Could an ice calorimeter be used to measure the heat absorbed by an endoergic reaction?

5 What is the purpose of the ice in the outer jacket of the ice-calorimeter? Would you expect it to be effective for this purpose?

6 Is there any way in which heat could be transferred from the surroundings into the inner ice, and thereby increase the weight of the water collected? Is there any way that Lavoisier and Laplace could have checked and allowed for such an error?

7 Suggest other possible sources of error in this method of measuring the heat evolved.

8 Lavoisier and Laplace *concluded* that the process of respiration was essentially the same process as the slow combustion of carbon. What is meant by a 'conclusion' in such a situation?

From this experiment of Lavoisier and Laplace it can be seen that in order to measure the energy changes associated with chemical reactions, it is necessary to have at least two things:

- units in which energy can be expressed;
- instruments by means of which the energy can be measured.

Units

Lavoisier and Laplace used the 'ounce' of ice melted as the 'unit' to indicate the quantity of heat evolved. In later times, the unit for quantity of heat in both chemistry and physics was the calorie.

More recently, it has been recommended at an international level that a new set of units be adopted by all scientists and all nations. In this new system of units the calorie is abandoned and the recommended unit for energy is the joule.

The **joule (J)** is defined as the amount of work that is done when a force of one newton (N) moves an object one metre (m) in the direction of the force:

$$4.184 \text{ joule} = 1 \text{ calorie}.$$

In this booklet, the energy associated with chemical and physical changes will be expressed in joule or kilo-joule.

A **kilo-joule (kJ)** is equal to 1000 joule.

Modern Calorimeters

Instead of using ice-calorimeters as Lavoisier and Laplace did, it is now more usual to measure the heat exchange of a chemical reaction by means of the temperature change produced in a known mass of water. The quantity of heat can then be calculated by means of the relationship:

Heat exchange = mass of water × change of temp. × specific heat of water

One instrument that can be used for this purpose is illustrated in figure 6.

The **bomb calorimeter** is used to measure the heat given out when organic solids and liquids—including foods and fuels—are burnt. The bomb is a cylindrical vessel made of steel; inside, there is a platinum crucible containing a known weight of the substance to be tested. Oxygen is pumped into the bomb, until a pressure of about twenty-five atmospheres is obtained. The sealed bomb is immersed in the known mass of water. A coil of very thin wire immersed in the material in the crucible is heated by the passage of an electric current. As the wire fuses, it ignites the test material and rapid combustion takes place. The rise in water temperature is noted. Allowances must be made for the fact that the bomb itself absorbs some of the heat; heat is given out by the passage of electricity through the wire and

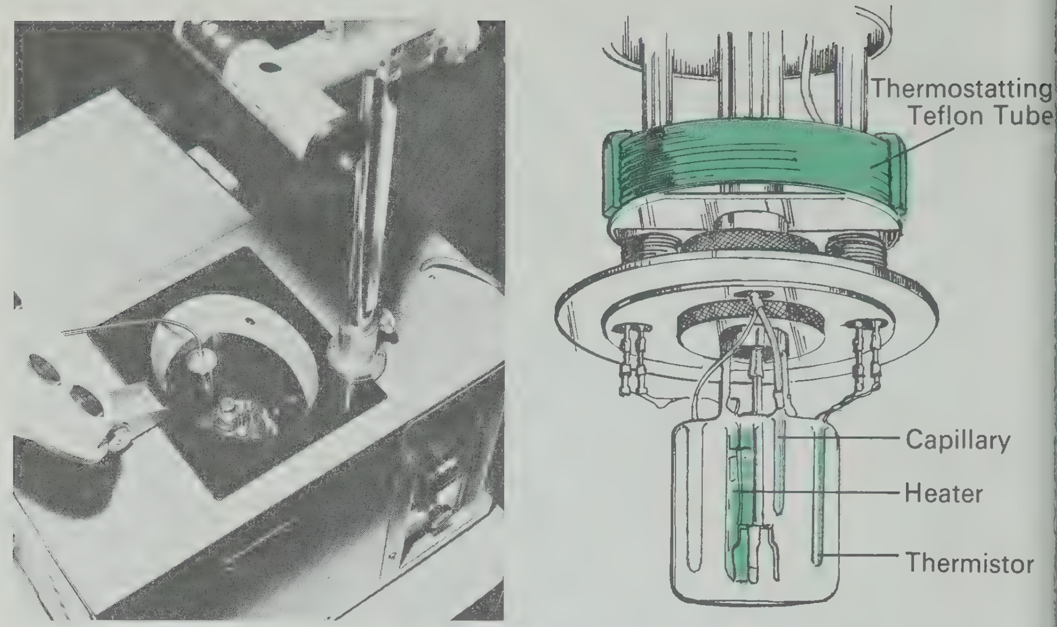


Figure 6. The bomb calorimeter

by the action of the stirring mechanism. Instead of making specific allowances for such items, the apparatus is usually standardized by burning a sample of a substance whose heat of combustion is already known.

An alternative method is to place a heating coil in the calorimeter and to generate a known amount of heat by the passage of an electric current. The heat capacity of the calorimeter and its accessories can be determined by either method.

Exercises

9 What sources of error would be significant in the bomb calorimeter?

10 The complete combustion of 1.500 g of hexane (C_6H_{14}) in a bomb calorimeter evolved 72.60 kJ of heat. Calculate the heat evolved by 1 mole of hexane under these conditions [Ans: 4171 kJ]

11 The complete combustion of 1.712 g of heptane (m.w. = 100.20) in a bomb calorimeter evolved 82.22 kJ of heat. Calculate the heat evolved by 1 mole of heptane under these conditions. [Ans: 4811 kJ]

12 To change the temperature of a particular calorimeter and the water it contained by one Celsius degree required 6.550 J. When 0.039 g of benzene (C_6H_6) was burnt in this constant volume system at 25°C, the temperature of the calorimeter and contents rose by 2.50 Celsius degrees. Calculate the heat evolved when one mole of benzene is burnt under these conditions. [Ans: 3275 kJ]

The Accuracy of Heat Measurements

Chemists have developed a high degree of accuracy in the measurement of the heat changes associated with chemical changes. This has been achieved by:

- taking great care to minimize transfer of heat;
- measuring the temperature change very carefully;
- carefully selecting the reaction to be studied.

The last point is important. If the reaction is very slow; if it does not proceed to completion; or if side reactions take place at the same time as the main reaction, attention to other details is fruitless. In general, combustion reactions satisfy the requirements, and heats of combustion have been determined very accurately. For example, the heat of combustion of n-butane is 2878.4 kJ mole^{-1}.

The accuracy of this measurement is indicated by the fact that the value is given to five significant figures. This means that the investigator is confident that the first four figures are correct, but is uncertain about the last figure.

If the investigator wished to indicate his possible error more precisely he would use another method of indicating his degree of uncertainty, e.g. 2878.4 ± 0.4 kJ. This indicates that the experimenter is confident that the correct value is between 2878.0 kJ and 2878.8 kJ.

There are various other types of calorimeters, each being adapted to its particular purpose, and in some cases to a particular type of reaction. A general difficulty is to minimize the transfer of heat into or out of the calorimeter. For very accurate measurements the calorimeter is surrounded by an outer jacket containing water. The temperature of this outer jacket is adjusted electrically during the course of the reaction so that it does not differ by more than one-tenth of a Celsius degree from that of the calorimeter. By this means transfer of heat to or from the calorimeter is kept to a minimum.

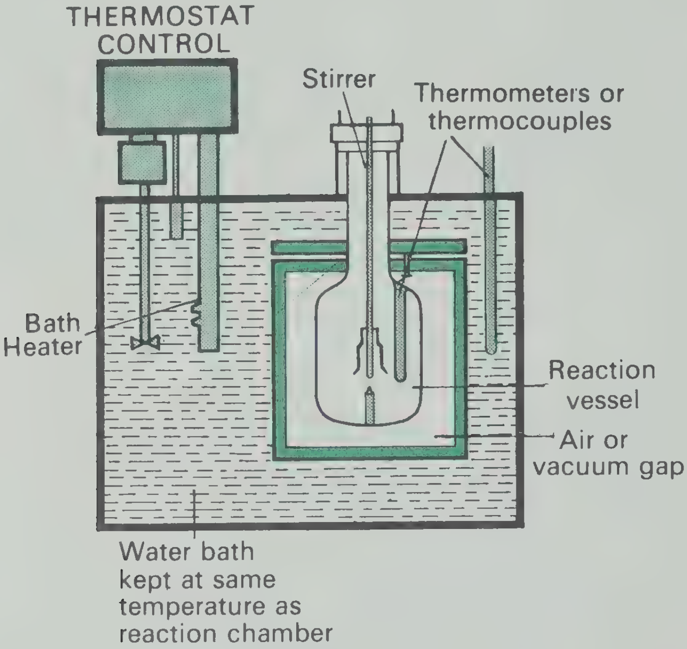

THERMOSTAT CONTROL
Stirrer
Thermometers or thermocouples
Bath
Heater
Reaction vessel
Air or vacuum gap
Water bath kept at same temperature as reaction chamber

Figure 7. A calorimeter in which the reaction vessel is surrounded by a temperature bath kept at the same temperature as the reaction vessel throughout the reaction

In each of these calorimeters a large quantity of water is used to absorb or release the heat. The advantage is that at the end of the reaction, the temperature of the products is only slightly different from that of the reactants at the start of the reaction. One can consider that the reaction has occurred at approximately constant temperature; this is of some importance in theoretical considerations. A disadvantage is the difficulty in accurately measuring the small change in temperature and special thermometers are needed for this.

PROBLEM

Suppose that in the school laboratory you are required to determine experimentally the heat change that takes place when two solutions are mixed.

(a) What apparatus would you select so as to minimize heat transfer?

(b) How would you determine the heat capacity of the reaction vessel?

(c) What thermometer would you select to measure the temperature change? To how many significant figures would you expect to read the temperature?

Solution

(a) Most schools possess a small Dewar vacuum flask (thermos flask) and failing this the styro-foam cups used as containers for hot tea or coffee give reasonable results for an appropriate reaction of solutions.

(b) Place a known mass of water in the reaction vessel and note its temperature. Warm an equal mass of water to approximately ten degrees above room temperature and note its temperature accurately. Add the known mass of this warm water to cooler water in the vessel, stir continuously and note the maximum rise in temperature.

Calculate the heat gained by the cool water and the heat lost by the hot water. The difference between this is the heat absorbed by the vessel and thermometer.

$$\text{heat capacity} = \frac{\text{heat absorbed by vessel and thermometer}}{\text{rise in temperature}}$$

(c) Obviously, the thermometer required is the one that will give the greatest accuracy at the appropriate temperature range. Many schools have thermometers reading from 0°C to 50°C with each degree subdivided into fifths, i.e. the temperature can be read to 0.2°C. If this is the thermometer used, then the temperature can be read to three significant figures. But the rise in temperature can probably only be read to two figures e.g.

23.*6*°C to 25.*2*°C; rise in temperature 1.*6*°C.

PROBLEM

Discuss the difficulties involved in measuring the heat change that takes place when iron rusts. How could the errors arising from these difficulties be minimized?

Solution

The main difficulties in this determination arise from:

- the slowness of the reaction since this would make it very difficult to prevent loss of heat to the surroundings;
- the difficulty of ensuring that the reaction proceeded to completion.

To minimize the error arising from the first factor it would be desirable to use maximum precautions to minimize transference of heat; to estimate the rate at which heat is being lost; and to speed up the reaction as much as possible. The reaction could be accelerated by having the iron with maximum surface area in contact with copper, and an ample supply of oxygen.

With regard to the second factor; at the completion of the measurement the weight of unchanged iron could be estimated by chemical means, and the weight of rusted iron calculated.

PROBLEM

(a) Why is measurement desirable in relation to scientific observations?

(b) Although measurement is very important to science, it is an exaggeration to suppose that important scientific discoveries cannot be made without measurement. List some important scientific discoveries which were not based—initially, at least—on quantitative observations.

Solution

(a) Measurement is important because:

- a quantitative observation is more precise and definite than a qualitative observation and conveys much more information;
- when observations are quantitative, the very powerful tool of mathematics can be applied to the results.

(b) Other things being equal, when a science becomes quantitative it increases man's understanding and control of the system studied; predictions are more certain and more precise.

Important scientific discoveries that were based upon qualitative observations include:

- magnetic effect of a current (Oersted, 1820);
- electricity by electromagnetic induction (Faraday, 1831);
- germ theory of disease (Pasteur, 1870-80);
- discovery of X-rays (Roentgen, 1896);
- discovery of radioactivity (Becquerel, 1896).

How Can Chemical Energy be Explained?

The potential energy of the water in the dams of the Snowy River Project can be explained in terms of the force of gravity; the energy of the wind can be explained by reference to convection currents caused by the heating effect of the sun. In what terms can the chemical energy stored in glucose or any other compound be explained?

Enthalpy

We can make one step towards an explanation if we accept that:

> a mole of each substance at a given temperature and pressure possesses a certain energy content which is just as characteristic of the substance as its molar mass. This energy content is sometimes called the **enthalpy** of the substance and is represented by the letter H.

On this basis, the energy evolved or absorbed by a chemical reaction is simply the **enthalpy change** (ΔH) of the system. (Δ is the Greek letter delta and when used before any quantity represents *the change* in this quantity.)

The enthalpy change (ΔH) is the difference between the total enthalpies of the products formed in a chemical reaction $\Sigma H_{(products)}$ and the total enthalpies of the reactants in that chemical reaction, $\Sigma H_{(reactants)}$. (Σ is the Greek letter sigma and represents the sum of the particular quantities indicated, in this case the enthalpies.)

In the reaction $A + B = C + D$:

the sum of the enthalpies of the reactants is
$H_a + H_b = \Sigma H_{(reactants)}$;

the sum of the enthalpies of the products is
$H_c + H_d = \Sigma H_{(products)}$;

ΔH = difference between $\Sigma H_{(products)}$ and $\Sigma H_{(reactants)}$

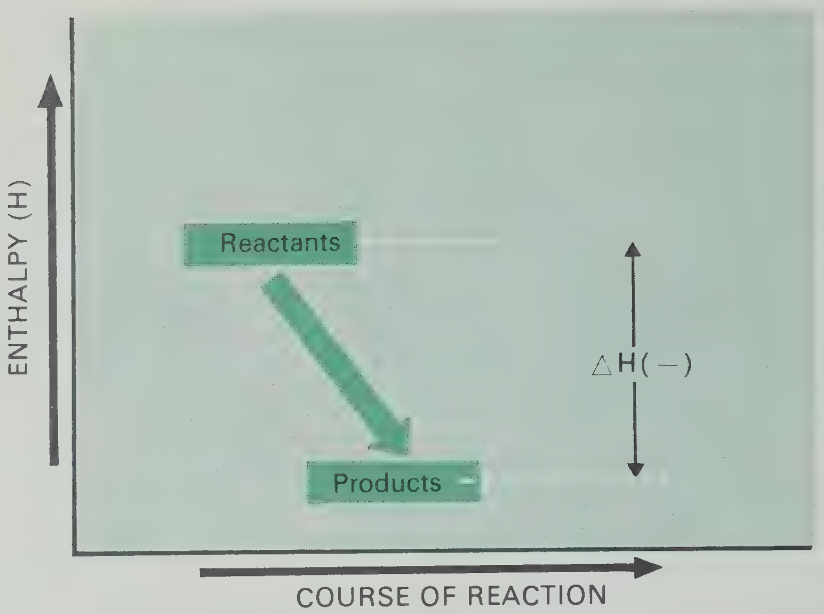


Figure 8. Enthalpy diagram for exoergic reactions

For an exoergic reaction:

- the sum of the enthalpies of the products is less than the sum of the enthalpies of the reactants. Energy is emitted.

$$\Sigma H_{(products)} < \Sigma H_{(reactants)}$$

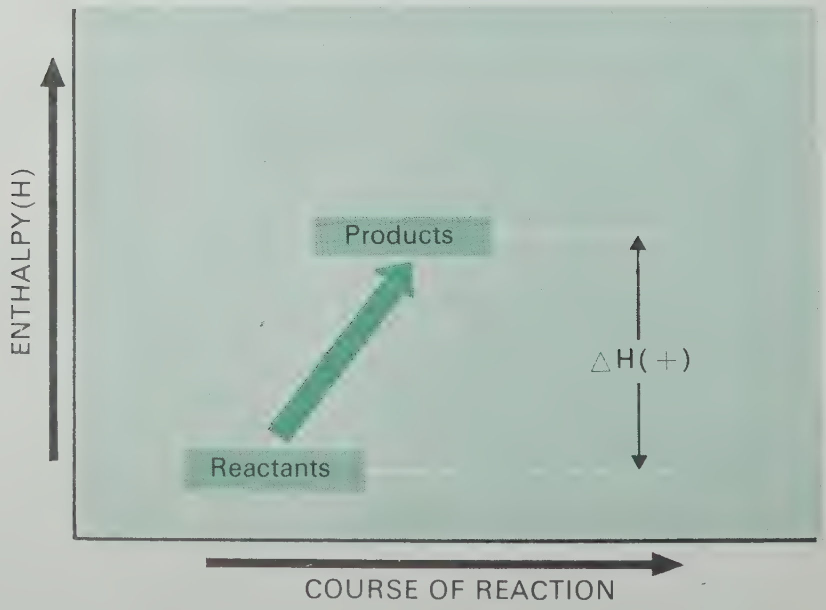


Figure 9. Enthalpy diagram for endoergic reactions

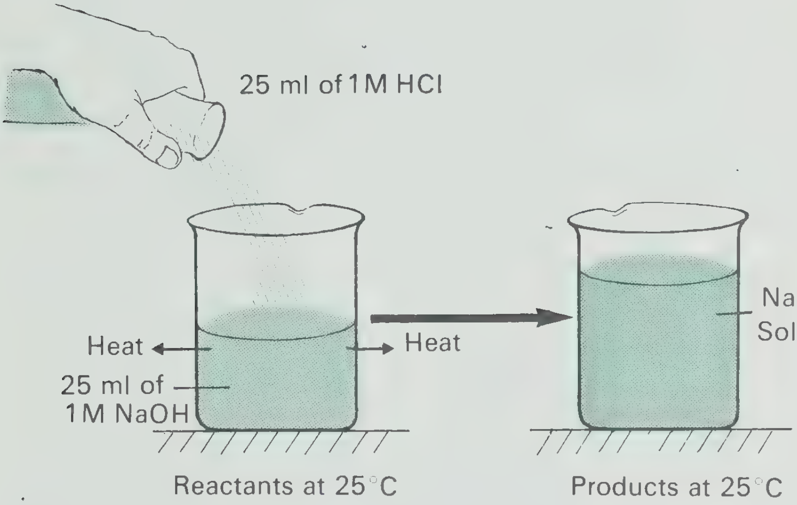
For an endoergic reaction:

- the sum of the enthalpies of the products is greater than the sum of the enthalpies of the reactants. Energy is absorbed.

$$\Sigma H_{(products)} > \Sigma H_{(reactants)}$$

Let us examine a simple chemical reaction to illustrate the concept of enthalpy change.

$$HCl + NaOH = NaCl + H_2O + Heat$$



$HCl + NaOH = NaCl + H_2O + Heat$

Figure 10. An exoergic reaction in a closed or open system loses energy to its surroundings

Before proceeding with further discussion of this chemical reaction new terms will be introduced. **The System** is that part of the universe which is under study in the particular system. **The Surroundings** are the rest of the universe.

Example

If we mix zinc and dilute hydrochloric acid in a test tube, we are interested in the contents of the test tube and for us, this is the system. The test tube, atmosphere and rest of the universe constitute the surroundings. An **open system** is one which can exchange matter and energy with the surroundings. The contents of a beaker which is standing on the laboratory bench is an example of an open system. A **closed system** is one which can gain or lose energy but cannot exchange matter with its surroundings. The contents of a sealed flask is an example of a closed system. An **isolated system** is one which cannot exchange matter or energy with its surroundings. Consequently, it is not affected by external effects. The contents of a sealed Dewar vacuum flask approximate to an isolated system.

In the example illustrated in figure 10, 25ml of 1M HCl solution at 25°C is placed in a beaker with 25ml of 1M NaOH solution at 25°C. Because of the heat of the reaction between the HCl and NaOH the contents of the beaker—the system—will become warm. Heat will be lost to the surroundings, until finally the system consists of a solution of sodium chloride at 25°C. Whenever any exothermic reaction is carried out in this way the system—the contents of the beaker—will lose heat to the surroundings. Because there is a *loss* of heat from the system, the heat change (ΔH) is said to be **negative.** When endothermic reactions are carried out in this manner, the system *gains* heat from the surroundings and the heat change is said to be positive.

In general, it can be said that:

- for exoergic changes ΔH is negative;
- for endoergic changes ΔH is positive.

From these conventions it follows that:

$$\text{energy change} = \left\{\begin{matrix}\text{sum of enthalpies}\\ \text{of the products}\end{matrix}\right\} - \left\{\begin{matrix}\text{sum of the enthalpies}\\ \text{of the reactants}\end{matrix}\right\}$$

$$\Delta H = \Sigma H_{(products)} - \Sigma H_{(reactants)}$$

The term enthalpy change (ΔH) strictly is only appropriate when the reaction is carried out at constant pressure. Most chemical reactions are carried out at atmospheric pressure which is approximately constant; but *reactions in the bomb calorimeter are not at constant pressure* and this instrument does not measure ΔH directly, although ΔH can be derived from the results.

The Causes of Enthalpy Changes in Chemical Reactions

The enthalpy or stored energy of a substance at a given temperature and pressure is the sum total of a number of different types of energy. These include:

- the energy due to the motion of the particles, i.e. the energy
- of translation, of rotation and vibration;
- the energy associated with the forces between the non-bonded particles, e.g. the van der Waals forces;
- the energy associated with the bonds between the atoms;
- the energy associated with the non-bonding electrons;
- the energy associated with the nuclei.

Monatomic gas	Diatomic gas
The stored energy (enthalpy) of the atoms of helium at 25°C is made up of the following:	The stored energy (enthalpy) of the atoms of oxygen at 25°C is made up of the following:
Kinetic energy due to translational motion	Kinetic energy due to translational, rotational and vibrational motion of the molecules
Potential energy due to weak forces of attraction between atoms	Potential energy due to the attractive forces between the molecules
Energy of the electrons in each atom (due to their motion and their position in the electric field) created by the positive charge of the nucleus and the negative charges of the electrons	Energy of the non-bonding electrons due to their motion and their position in the electric field created by the positive charge of the nucleus and the negative charges of the electrons
Energy associated with the nuclei	Energy associated with the nuclei
	Energy associated with the bonding electrons

In any chemical change, the stored energies associated with atomic nuclei and the non-bonding electrons do not change appreciably. The energy changes associated with the forces between particles and the kinetic energy of the particles are small. This implies that the greatest change in energy is associated with the breaking and formation of chemical bonds.

As a first approximation it can be said that the energy change of a chemical change is the sum total of the energy derived from the breaking and formation of bonds.

Thermochemical Equations

Energy changes can be represented by including the energy term in the normal word or symbolic equation, as though the energy were a reactant or product.

Examples

Combustion:

$$\text{carbon} + \text{oxygen} \longrightarrow \text{carbon dioxide} + \text{heat energy}$$
$$C + O_2 = CO_2 + 393.4\ \text{kJ}$$

Daniell cell reaction:
zinc + copper sulphate ⟶ copper + zinc sulphate ± electrical energy

Reduction of haematite

$$3C + 2Fe_2O_3 + 463\text{ kJ} = 4Fe + 3CO_2$$

More frequently, the energy changes are indicated by adding the ΔH notation to the symbolic equation.

Examples

Combustion of sulphur:

$$S + O_2 = SO_2 \qquad \Delta H = -296\text{ kJ}$$

Formation of quicklime:

$$CaCO_2 = CaO + CO_2 \qquad \Delta H = +177.8\text{kJ}$$

The magnitude of ΔH depends to some extent, on the temperature and pressure at which the reaction takes place. It is usual to give the value of ΔH for standard conditions, i.e. 25°C (298K) and standard atmospheric pressure. For these conditions the energy change is represented by ΔH°_{298} where the superscript ° represents standard atmospheric pressure, and the subscript $_{298}$, represents standard temperature in degrees Kelvin.

The magnitude of ΔH depends also upon the physical state of each reactant and product; therefore, to make the statement precise it is necessary to specify these states in the equation. This is usually done by means of subscripts:

(*s*) for solid	(*g*) for gas
(*l*) for liquid	(*aq*) dissolved in a large volume of water.

Examples

Combustion of glucose

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} = 6CO_{2(g)} + 6H_2O_{(l)} \quad \Delta H^\circ{}_{298} = -2186\text{ kJ}$$

Daniell cell reaction:

$$Zn_{(s)} + CuSO_{4(aq)} = ZnSO_{4(aq)} + Cu_{(s)} \qquad \Delta H^\circ_{298} = -216.7\text{ kJ}$$

Finally, it is also necessary to specify the particular form of the solid, because different forms of the same solid may differ in their enthalpy.

Examples

Combustion of graphite:

$$C_{(graphite)} + O_{2(g)} = CO_{2(g)} \qquad \Delta H^{\circ}_{298} = -394\ \text{kJ}$$

Combustion of diamond:

$$C_{(diamond)} + O_{2(g)} = CO_{2(g)} \qquad \Delta H^{\circ}_{298} = -396\ \text{kJ}$$

Exercises

Unless otherwise stated all changes mentioned in the questions below are to be considered as taking place in a closed system at constant pressure.

13 Indicate which of the following changes are exoergic and which endoergic.

(a) Combustion of magnesium:

$$Mg_{(s)} + \tfrac{1}{2}O_{2(g)} = MgO_{(s)} \qquad \Delta H^{\circ}_{298} = -601.5\ \text{kJ}$$

(b) Formation of nitrogen dioxide:

$$N_{2(g)} + 2O_{2(g)} = 2NO_{2(g)} \qquad \Delta H^{\circ}_{298} = +67.4\ \text{kJ}$$

(c) Dissociation of hydrogen:

$$H_{2(g)} = 2H_{(g)} \qquad \Delta H^{\circ}_{298} = +432\ \text{kJ}$$

14 Indicate for each of the following changes whether the total enthalpy is greater for the reactants or for the products:

(a) electrolysis of water,
(b) slaking of lime,
(c) cracking of kerosene,
(d) sublimation of dry ice,
(e) discharge of a dry cell,
(f) explosion of T.N.T.,
(g) decomposition of dead organism,
(h) respiration.

15 Indicate whether ΔH is positive or negative for each of the following changes:

(a) condensation of steam,
(b) sublimation of iodine,
(c) electrolysis of magnesium chloride,
(d) action of light on photographic film.

16 Rewrite the following thermochemical equations so that they *represent* only one *mole* of the underlined substance.

(a) $2H_{2(g)} + O_{2(g)} = 2H_2O_{(l)} \qquad \Delta H^{\circ}_{298} = -572\ \text{kJ}$
(b) $N_{2(g)} + O_{2(g)} = 2NO_{(g)} \qquad \Delta H^{\circ}_{298} = +180.76\ \text{kJ}$
(c) $H_{2(g)} = 2H \qquad \Delta H^{\circ}_{298} = +436\ \text{kJ}$
(d) $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)} \qquad \Delta H^{\circ}_{298} = -91.8\ \text{kJ}$

17 Using a diagram, explain the difference in the enthalpy changes for the following reactions:

(a) $H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(l)} \qquad \Delta H^{\circ}_{298} = -286\ \text{kJ}$

(b) $H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)} \qquad \Delta H^{\circ}_{298} = -242\ \text{kJ}$

18 Draw enthalpy diagrams for the following reactions:

(a) Formation of ozone:
$\frac{3}{2}O_{2(g)} = O_{3(g)} \qquad \Delta H^{\circ}_{298} = +142.3\ \text{kJ}$

(b) Rusting of iron:
$2Fe_{(s)} + \frac{3}{2}O_{2(g)} = Fe_2O_{3(s)} \qquad \Delta H^{\circ}_{298} = -820.2\ \text{kJ}$

(c) Atomization of chlorine:
$Cl_{2(g)} = 2Cl_{(g)} \qquad \Delta H^{\circ}_{298} = +243.8\ \text{kJ}$

(d) Electrolysis of magnesium chloride:
$MgCl_{2(s)} = Mg_{(s)} + Cl_{2(g)} \qquad \Delta H^{\circ}_{298} = +641.8\ \text{kJ}$

19 In what forms does the enthalpy or stored energy exist in ice at —10°C?

If heat is supplied to produce the following changes, suggest the form or forms of energy that have been increased in each case:

(a) ice at —10°C ⟶ ice at 0°C;
(b) ice at 0°C ⟶ water at 0°C;
(c) water at 0°C ⟶ water at 100°C;
(d) water at 100°C ⟶ steam at 100°C;
(e) steam at 100°C ⟶ steam at 200°C (pressure constant);
(f) steam at 100°C ⟶ steam at 200°C (volume constant).

20 Is the enthalpy of water at 0°K zero? Discuss.

Is Chemical Energy Conserved?

Scientific Laws

The word law is not always used with a consistent meaning in science but, in most cases, it is a generalization derived directly from experimental or observed results.

The Law of Conservation of Mass which states:

> **"In any physical or chemical change no matter is created or destroyed",**

sums up the results of experiments by scientists who have very carefully weighed materials before and after a variety of physical and chemical changes.

It is now accepted that, despite its basis of consistent and accurate experimental data, the Law of Conservation of Mass needs re-interpretation. This is because of the acceptance of Albert Einstein's theory that energy and mass are equivalent, the relationship between the two being expressed by the formula $E = mc^2$. This implies that when energy is given out in an exoergic reaction the mass of the products is slightly less than that of the reactants. Again, in an endoergic reaction it is expected that the products gain slightly in mass because of the energy absorbed. In both cases, the change in mass is too small to be detected by even the most accurate balance.

A more detailed discussion of Einstein's mass-energy equivalence formula ($E = mc^2$) is discussed in the NSCM Booklet C1, A Chemist's View of the Atom. In nuclear reactions which are discussed later in this booklet, the mass-energy relationship becomes significant.

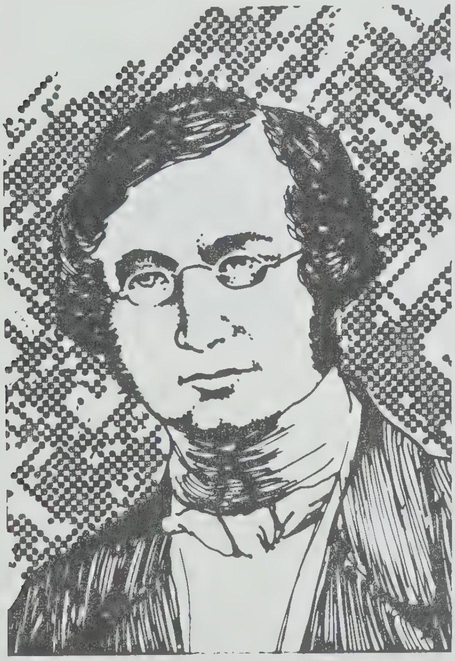


Figure 11. Julius Robert von Mayer (1814-1868) was a German physician. In 1840 he went as ship's doctor on a voyage to Java. While bleeding patients in Java, he noticed the unusual brightness of the venous blood; he related this to the lower rate of respiration in the tropics and this led him to the consideration of the nature of heat and to the conclusion that it and mechanical work (energy) were equivalent. He later became a practising medical doctor in his home town of Heilbronn; his townsmen ridiculed his intellectual ability, and the mental agony caused by this rejection upset Mayer so much that he was for a time confined in a mental hospital.

The First Law of Thermodynamics

The first law of thermodynamics is the Law of Conservation of Energy, which states that:

> Energy cannot be created or destroyed but can be changed from one form to another.

It has a history which illustrates that scientists have a very strong intuitive belief in conservation of energy, or more generally in what Mayer called 'the general law of indestructibility of causes'. This strong intuitive belief has led them to broaden, and thereby preserve, the conservation law whenever it appeared to break down. The concept of conservation was applied firstly to the early concepts of what we now call kinetic energy and then extended to include potential energy. It was applied independently to heat and in this area was widened by Black, to include latent heat. When Rumford and Joule found that heat and mechanical energy were equivalent, the law was broadened to cover both; later still it was interpreted to include all forms of energy. At present, the law must be interpreted to take into account Einstein's mass-energy equivalence. The statement '*energy is conserved*' is acceptable so long as it is remembered that mass is one form of energy.

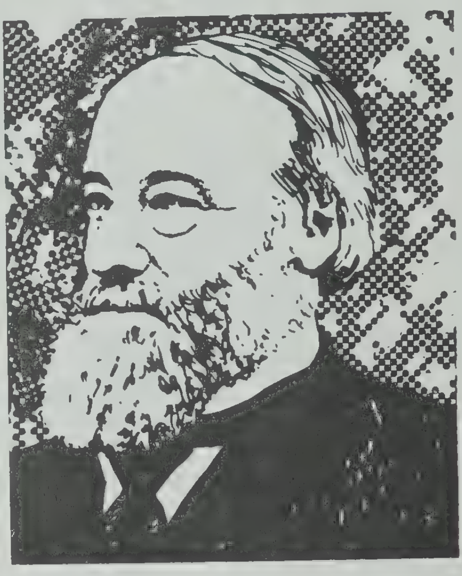


Figure 12. James Prescott Joule (1818-1889) was the son of a wealthy brewery owner in Manchester, England. He studied mathematics and science under John Dalton. A superb experimenter, he produced the first accurate experimental results to justify the equivalence of heat and mechanical work. He was one of the developers of the kinetic theory of gases. His name is given to the electrical unit of work, the joule.

For an exoergic change:

$$\left\{\begin{matrix}\text{energy equivalent of}\\\text{mass of reactants}\end{matrix}\right\} = \left\{\begin{matrix}\text{energy equivalent of}\\\text{mass of reactants}\end{matrix}\right\} + \left\{\text{energy evolved}\right\}$$

For an endoergic change:

$$\left\{\begin{matrix}\text{energy equivalent of}\\\text{mass of reactants}\end{matrix}\right\} + \left\{\begin{matrix}\text{energy}\\\text{absorbed}\end{matrix}\right\} = \left\{\begin{matrix}\text{energy equivalent of}\\\text{mass of products}\end{matrix}\right\}$$

Because matter and energy are now accepted as equivalent, the Law of Conservation of Energy is identical with the Law of Conservation of Mass. It is not necessary to have the two statements; either is sufficient provided that it is interpreted to include both mass and energy. However, it is convenient to retain the two statements, because separately they can be applied within certain limits of accuracy.

Chemistry and the Conservation of Energy

The two forms of the Law of Conservation of Energy most useful in chemistry were stated independently by chemists.

Lavoisier and Laplace in 1780 stated, as self-evident, that as much heat is required to decompose a compound as is liberated when the compound is formed from its elements.

Interpreting this more generally, if the chemist finds that for the reaction $A + B \longrightarrow C + D$, the enthalpy change is $\Delta H = +100 \text{kJ mol}^{-1}$, he knows that for the reverse reaction $C + D \longrightarrow A + B$, the enthalpy change has the same magnitude but is the opposite sign i.e. $\Delta H = -100 \text{ kJ mol}^{-1}$.

Example

If the combustion of one mole of aluminium *evolves* 838 kJ of energy:

$$\text{i.e. } Al + \tfrac{3}{4}O_2 = \tfrac{1}{2}Al_2O_3 \qquad \Delta H = -838 \text{ kJ mol}^{-1},$$

then the same quantity of energy must be *supplied* to decompose the aluminium oxide formed.

$$\tfrac{1}{2}Al_2O_3 = Al + \tfrac{3}{4}O_2 \qquad \Delta H = +838 \text{ kJ mol}^{-1}.$$

The Law of Constant Heat Summation

In 1840 G. H. Hess (1802-1850), a Swiss chemist, as a result of his experimental work put forward the Law of Constant Heat Summation which states that:

'The change in heat content accompanying a chemical reaction is independent of the pathway between the initial and final states. The resultant heat change in a chemical change is the same whether it takes place in one or several stages.' (This is sometimes called Hess's Law.)

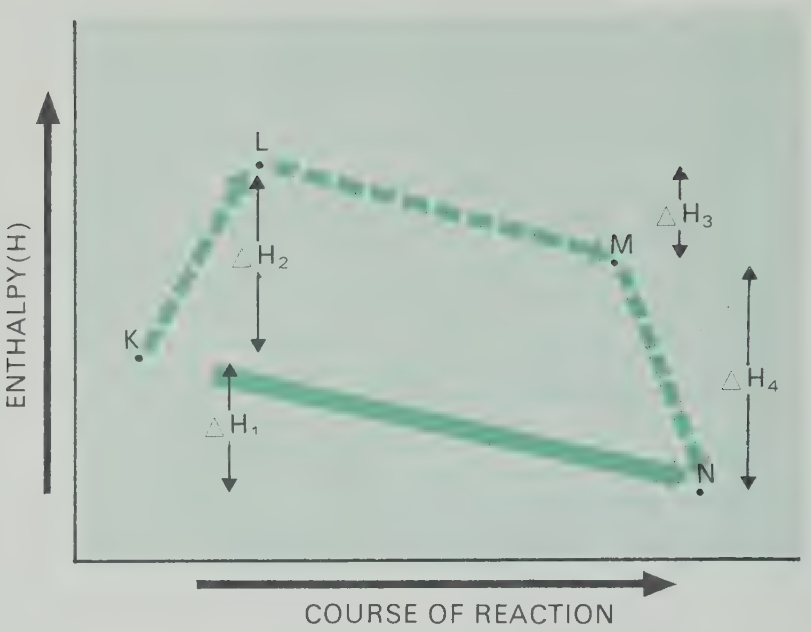


Figure 13. Enthalpy diagram to illustrate Hess's Law: $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$.

This law implies that the net change in enthalpy is the same, whether reactants K, are converted to products N, directly or through a series of intermediate steps. (See figure 13.)

The enthalpy change (ΔH_1) for the direct change equals the algebraic sum of the enthalpy changes of the intermediatary steps $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$ (taking due account of the signs of these quantities).

Example

It is possible to convert carbon to carbon dioxide directly:

$$C_{(graphite)} + O_{2(g)} = CO_{2(g)} \qquad \Delta H_1 = -394\ \text{kJ mol}^{-1}$$

or indirectly by forming carbon monoxide and then converting this to carbon dioxide.

$$C_{(graphite)} + \tfrac{1}{2}O_{2(g)} = CO_{(g)} \qquad \Delta H_2 = ?$$

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} = CO_{2(g)} \qquad \Delta H_3 = -283\ \text{kJ mol}^{-1}$$

In this reaction, while ΔH_1 and ΔH_3 are comparatively easy to measure, ΔH_2 is difficult to measure. ΔH_2 may be calculated by applying the Law of Constant Heat Summation.

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

$$\begin{aligned} \Delta H_2 &= \Delta H_1 - \Delta H_3 \\ &= (-394 \text{ kJ mol}^{-1}) - (-283 \text{ kJ mol}^{-1}) \\ &= -111 \text{ kJ mol}^{-1} \end{aligned}$$

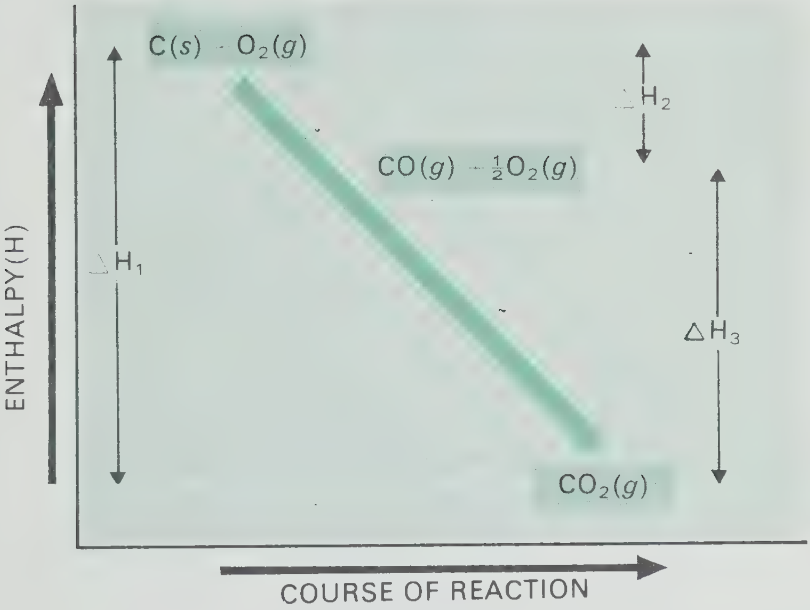


Figure 14. Enthalpy diagram to illustrate the derivation of the heat of combustion of carbon monoxide

Another way of using the Law of Constant Heat Summation to calculate heats of reactions relies on the fact that the law implies that chemical equations can be treated as algebraic equations.

Example

(i) $C_{(graphite)} + O_{2(g)} = CO_{2(g)} \quad \Delta H^\circ_{298} = -394 \text{ kJ mol}^{-1}$

(ii) $2H_{2(g)} + O_{2(g)} = 2H_2O_{(l)} \quad \Delta H^\circ_{298} = -572 \text{ kJ mol}^{-1}$

(iii) $CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} = CO_{2(g)} + 2H_2O \quad \Delta H^\circ_{298} = -710 \text{ kJ mol}^{-1}$

Using the above theremochemical equations, find the enthalpy change (heat of reaction) for the following synthesis of methanol:

(iv) $C + 2H_2 + \frac{1}{2}O_2 = CH_3OH$

From observation equation (iv) can be obtained by reversing equation (iii) and adding to it the addition of equations (i) and (iii).

i.e. (iv) = (i) + (ii) − (iii)

Applying this to the heats of reaction, the heat of reaction for equation (iv)

$= (-394 \text{ kJ mol}^{-1}) + (-572 \text{ kJ mol}^{-1}) - (-710 \text{ kJ mol}^{-1}),$

$= -256 \text{ kJ mol}^{-1}$

Therefore:

$$C_{(graphite)} + 2H_{2(g)} + \tfrac{1}{2}O_{2(g)} = CH_3OH_{(l)} \qquad \Delta H^\circ_{298} = -256 \text{ kJ mol}^{-1}$$

Exercises

$C_{(graphite)} + O_2 = CO_2 \quad \Delta H^\circ_{298} = -394 \text{ kJ mol}^{-1}.$

$C_{(diamond)} + O_2 = CO_2 \quad \Delta H^\circ_{298} = -396 \text{ kJ mol}^{-1}.$

$H_{2(g)} + \frac{1}{2}O_2 = H_2O \quad \Delta H^\circ_{298} = -286 \text{ kJ mol}^{-1}.$

$2HgO = 2Hg + O_2 \quad \Delta H^\circ_{298} = -181.6 \text{ kJ mol}^{-1}.$

$3C_{(graphite)} + 2Fe_2O_3 = 3CO_2 + 4Fe \quad \Delta H^\circ_{298} = 464 \text{ kJ mol}^{-1}.$

$C_{(graphite)} + \frac{1}{2}O_2 = CO \quad \Delta H^\circ_{298} = -110.5 \text{ kJ mol}^{-1}.$

In the following questions use the thermochemical equations above.

21 Write thermochemical equations to illustrate:
(a) the electrolysis of two moles of water
(b) the union of one mole of mercury with oxygen.

22 Calculate the enthalpy change for production of water gas ($CO + H_2$), according to the equation:

$$C_{(graphite)} + H_2O_{(l)} = CO_{(g)} + H_{2(g)}$$

[Ans: $\Delta H^\circ_{298} = +175.5$ kJ]

23 Calculate the enthalpy change for the production of diamonds from graphite. In view of your answer, how do you account for the great difficulty experienced in making diamonds from graphite?

[Ans: $\Delta H^\circ_{298} = +2$ kJ]

24 Calculate the enthalpy change for the production of one mole of iron oxide (Fe_2O_3) from its constituent elements.

[Ans: $\Delta H^\circ_{298} = -823$ kJ]

How are Chemical Energy Data Organized and Used?

The results of the measurements of chemical energy are usually included in physical and chemical data books. No book could appear to be duller or less inspiring than a data book; thousands of pages of numerical values listed in small print under symbols or abbreviations which are unintelligible to all except the specialists. Yet, considered from another point of view a data book is a monument as awe-inspiring as any of the monuments that attract crowds of visitors in a variety of nations. Sydney is already proud of its Opera House and the citizens point with pride to the skill, ingenuity and industry that is creating it. On each of these counts it is insignificant compared to a data book; the information packed into such a book has been built up laboriously over centuries by men and women of all colours and of all nations, men and women of outstanding accuracy, perserverence and ingenuity.

A single item in the data book may represent years of tedious, patient work by one or more scientists. No matter how difficult or time-consuming the measurement, the item is made available for all to use without cost or restriction. The only requirement is that the would-be user understands the information and how to employ it. In the following section a few lists of such data relevant to the topic of chemical energy will be considered; these are certain types of enthalpy changes which are listed, quoted and used so frequently that they merit special attention. Heats of combustion, solution, fusion, vaporization, sublimation and atomization will be illustrated and discussed briefly.

Standard Heat of Combustion

The standard heat of combustion ($\Delta H^\circ c$) is the energy change which takes place when one mole of the substance is completely burnt in oxygen under standard conditions.

Example

The standard heat of combustion of hydrogen is -242.0 kJ mol^{-1}, when one mole of hydrogen reacts with oxygen under standard conditions, 242.0 kJ of heat is evolved.

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} = H_2O_{(l)} \qquad \Delta H^\circ_{298} = -242.0 \text{ kJ}$$

Table 1. Selected heats of combustion (ΔH_c° in kJ mol^{-1})

	ΔH_c° $kJmol^{-1}$
aluminium $Al_{(s)}$	—838
diborane B_2H_6	—2027
carbon (graphite) $C_{(s)}$	—394
carbon (diamond) $C_{(s)}$	—396
carbon monoxide $CO_{(g)}$	—283
methane $CH_{4(g)}$	—889
ethane $C_2H_{6(g)}$	—1557
n-butane $C_4H_{10(g)}$	—2874
n-pentane $C_5H_{12(l)}$	—3509
n-octane $C_8H_{18(l)}$	—5464
ethene (ethylene) $C_2H_{4(g)}$	—1410
ethyne (acetylene) $C_2H_{2(g)}$	—1299
benzene $C_6H_{6(l)}$	—3267
methyl benzene (toluene) $C_7H_{8(l)}$	—3916
methanol $CH_3OH_{(l)}$	—726
ethanol $C_2H_5OH_{(l)}$	—1367
glucose $C_6H_{12}O_{6(s)}$	—2816
sucrose $C_{12}H_{22}O_{11(s)}$	—5643
hydrogen $H_{2(g)}$	—286
phosphorus (white) $P_{(s)}$	–746
phosphorus (red) $P_{(s)}$	–728

Frequently the heat of combustion is defined as the 'heat evolved', and consequently is listed as a positive value. It is correct to record it as a negative value, to indicate that the system has lost energy.

Most, but not all, of the heats of combustion have been determined experimentally. As the number of significant figures indicates, many of them—particularly those of compounds used as fuels— have been determined to a high degree of accuracy. Because of their accuracy, and because from them other heats of reaction—including heats of formation—can be derived, heats of combustion occupy a very important place in the store of thermochemical data.

Exercises

25 Write the appropriate thermochemical equations to represent:
(a) the standard heat of combustion of ethane which is —1557 kJ mol^{-1}.,
(b) the standard heat of combustion of aluminium which is —838 kJ mol^{-1}.

26 How much energy can be obtained by the combustion of:
(a) 0.5 mole of n-butane;
(b) 10 g of hydrogen;
(c) 100 g of n-octane.
[Ans: (a) 1438.7 kJ (b) 1430 kJ (c) 4780 kJ]

27 Which would give the greater yield of heat when burnt under standard conditions:
(a) 1 g of ethane (b) 1 g of ethyne (acetylene).
Why is the acetylene used for cutting and welding in industry in preference to ethane?

28 Compare hydrogen and diborane (B_2H_6) as suitable rocket fuels on the basis of energy released per unit weight.

29 Explain the different heats of combustion for white phosphorus and red phosphorus. Use an enthalpy diagram to illustrate your answer.

Standard Heat of Neutralization

The standard heat of neutralization (ΔH°_n) of an acid or alkali is the energy change that takes place when that amount of the acid or alkali needed to form one mole of water, is neutralized at 25°C.

Example

The standard heat of neutralization of sulphuric acid is —55.89 kJ:

$$\tfrac{1}{2}H_2SO_{4(aq)} + NaOH_{(aq)} = \tfrac{1}{2}H_2SO_{4(aq)} + H_2O \qquad \Delta H_n = -55.89\text{ kJ}.$$

The following examples illustrate that neutralization is always exoergic and the magnitude of the heat evolved is approximately constant when the reactants are dilute solutions of strong acid and alkali.

Table 2. Selected heats of neutralization (Equal volume of reactants, each 1M concentration)

	ΔH^0_n kJmol^{-1}.
$HCl + NaOH = NaCl + H_2O$	—57.97
$HBr + NaOH = NaBr + H_2O$	—57.57
$HNO_3 + NaOH = NaNO_3 + H_2O$	—57.57
$CH_3COOH + NaOH = CH_3COONa + H_2O$	—56.15
$HCl + NH_3 = NH_4Cl$	—53.39
$CH_3COOH + NH_3 = CH_3COONH_4$	—50.38

Exercise

30 How much heat is evolved when:
(a) 50 ml of M HCl is neutralized by 50 ml of M NaOH;
(b) 100 ml of 2M HBr is neutralized by 100 ml of 2M NaOH;
(c) a solution containing 0.4 g of NaOH is neutralized by an equivalent weight of strong acid;
(d) a solution containing 100 g of acetic acid is neutralized by an equivalent weight of strong alkali.
[Ans: (a) 2.9 kJ (b) 11.5 kJ (c) 5.8 kJ (d) 93.7 kJ]

The Heat of Solution

The heat of solution (ΔH°_{sd}) of a substance is the energy change which takes place when one mole of the substance is completely dissolved (under standard conditions) in a volume of water such that no energy change takes place on further dilution. Such a solution is said to be at infinite dilution.

Example

The heat of solution of sulphuric acid is —74.2 kJ mol^{-1}, i.e. when one mole of sulphuric acid is dissolved in water to infinite dilution, 74.2 kJ of heat is evolved.

$$H_2SO_{4(l)} + (aq) \longrightarrow H_2SO_{4(aq)} \qquad \Delta H_{sol} = -74.2\ \text{kJ mol}^{-1}$$

From a study of table 3 it can be seen that when some substances dissolve in water, heat is evolved; but in other cases heat

Table 3. Selected heats of solution (ΔH°_{sol} in kJ mol^{-1})

hydrogen chloride $HCl_{(g)}$	—73.0
hydrogen bromide $HBr_{(g)}$	—82.9
hydrogen iodide $HI_{(g)}$	—80.1
sulphur dioxide $SO_{2(g)}$	—35.5
sulphur trioxide $SO_{3(g)}$	—156
ammonia $NH_{3(g)}$	—35.5
sulphuric acid $H_2SO_{4(l)}$	—74.2
nitric acid $HNO_{3\,(l)}$	—36.9
sodium hydroxide $NaOH_{(s)}$	—43.1
sodium chloride $NaCl_{(s)}$	+5.4
sodium nitrate $NaNO_{3(s)}$	+21.0
copper sulphate (hyd.) $CuSO_4.5H_2O_{(s)}$	+11.7
sodium thiosulphate $Na_2S_2O_{3(s)}$	+7.15
ammonium chloride $NH_4Cl_{(s)}$	+22.59

is absorbed. For example, ammonia dissolves with evolution of heat, but when hypo (sodium thiosulphate) dissolves the process is endoergic.

In accordance with the rule stated by Lavoisier and Laplace, reversing the process of solution reverses the sign of the energy change. For example, when ammonia escapes from solution heat is absorbed, and when hypo ($Na_2S_2O_3$) crystallizes from a saturated solution heat is liberated.

Exercises

31 Write the appropriate thermochemical equation to illustrate the heats of solution of:
(a) ammonia,
(b) hypo (sodium thiosulphate).

32 Explain in detail why it is dangerous to add water to sulphuric acid.

33 Foot warmers that are sometimes placed in trains are metal containers filled with a saturated solution of hypo. Explain how they function.

Latent Heats

The Molar Heat of Fusion

The molar heat of fusion (ΔH°_{fus}) at the melting point is the heat required at this temperature to convert one mole of the substance from solid to liquid without change of temperature.

Example

The molar heat of fusion of iron is 14 kJ mol⁻¹:

$$Fe_{(s)} \longrightarrow Fe_{(l)} \qquad \Delta H^\circ_{fus} = 14 \text{ kJ mol}^{-1}.$$

The Molar Heat of Vaporization

The molar heat of vaporization (ΔH°_v) is the heat required to convert one mole of the substance from the liquid to vapour, at the specified temperature and at one atmosphere pressure.

Example

The molar heat of vaporization of water at 25°C is 44 kJ mol⁻¹:

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H^\circ_v = 44 \text{ kJ mol}^{-1}$$

The Molar Heat of Sublimation

The molar heat of sublimation (ΔH°_s) is the heat required to convert one mole of the substance from the solid state to vapour, at the specified temperature and at one atmosphere pressure.

Example

The molar heat of sublimation of iodine at 25°C is 29 kJ mol⁻¹:

$$I_{2(s)} \longrightarrow I_{2(g)} \qquad \Delta H^\circ_s = 29 \text{ kJ mol}^{-1}$$

The Molar Heat of Atomization

The molar heat of atomization (ΔH°_{at}) is the energy required to convert one mole of the substance in its normal state under standard conditions to gaseous atoms still under the same conditions (25°C and one atmosphere pressure).

Example

The molar heat of atomization of iodine is 107 kJ. This amount of energy will convert iodine from its solid state of I_2 molecules at 25°C, to gaseous atoms at the same temperature, i.e.

$$I_{2(s)} \longrightarrow 2I_{(g)} \qquad \Delta H^\circ_{at} = 107 \text{ kJ mol}^{-1}$$

Table 4. Latent heats and heats of atomization

	ΔH_{fus} at m.p. kJ mol $^{-1}$	ΔH_v at b.p. kJ mol $^{-1}$	ΔH^0_{at} at 25°C kJ mol $^{-1}$
hydrogen	0.06	0.45	218
boron	22	510	573
carbon	—	—	718.4
oxygen	0.22	0.34	248
sodium	2.6	99.2	109
magnesium	8.8	128	150
aluminium	10	291	314
sulphur	1.2	10	279
chlorine	3.2	10.2	121
calcium	9.2	167	192
iron	14	351	418
copper	13	305	339
zinc	7.36	115	131
iodine	7.87	20.8	107
water	6.02	41	—
hydrogen sulphide	2.5	18.7	—
benzene	9.83	30.8	—
sodium chloride	29	170	—
magnesium chloride	43.1	—	—

Note: In this table the enthalpy change for the elements is that for one mole of *atoms*.

From the table, it can be noted that for any one element (with the exception of carbon) it is a general rule that

Molar Heat of Fusion	<	Molar Heat of Vaporization	<	Molar Heat of Atomization
ΔH°_{fus}	<	ΔH°_v	<	ΔH°_{at}

This generalization can be understood if the following points are kept in mind:

- all of these changes require the supply of energy;
- the energy supplied must be doing work against forces within the substance, i.e. particles may be moved apart against the attractive forces;
  (Note: work done = force × distance.)

where the energy required for a change is greater than that required for another, either the attractive force to be overcome is greater or the distance that the particles are separated is greater.

In general, the attractive forces that have to be overcome in passing from a solid to a liquid are of the same nature and magnitude as those that have to be overcome in passing from liquid to vapour. The greater magnitude of the heats of vaporization compared to the heats of fusion is attributed to the fact that the particles are separated through much greater distances in forming the vapour; the expansion of volume is much greater in vaporization than in melting.

In atomization on the other hand, where the value of the heat of atomization is much greater than the heat of vaporization, this is due frequently to the different type of force that has to be overcome, i.e. the force associated with the covalent bond.

Exercises

34 Write the thermochemical equations to represent the following statements:
(a) the heat of fusion of sodium chloride is 28 kJ;
(b) the heat of vaporization of sodium is 99 kJ;
(c) the heat of sublimation of carbon is 876 kJ;
(d) the heat of atomization of iodine is 109 kJ.

35 What type of forces must be overcome to:
(a) melt sulphur;
(b) vaporize copper;
(c) atomize hydrogen chloride;
(d) atomize zinc.

36 Calculate the energy required to:
(a) melt 100 g of aluminium;
(b) vaporize 152 g of benzene;
(c) atomize 1.00 g of sulphur;
(d) sublime 1.000 g of carbon.
[Ans: (a) 37 kJ; (b) 72.5 kJ (c) 8.69 kJ; (d) 68.0 kJ]

37 Explain the following:
(a) ΔH_{fus} of iron $>$ ΔH_{fus} of sulphur;
(b) ΔH_{fus} of sodium chloride $>$ ΔH_{fus} of benzene;
(c) ΔH_{fus} of magnesium chloride $>$ ΔH_{fus} of sodium chloride;
(d) ΔH_v of water $>$ ΔH_v of hydrogen sulphide;
(e) ΔH_{at} of carbon $=$ ΔH_s of carbon.

Standard Enthalpies of Formation and Bond Energies

Some important theoretical ideas have been developed from the systematic consideration of the measurements of chemical energy. These concepts enable the chemist to summarize in a more concise and useful form, large sections of thermochemical data; moreover, they provide a powerful means of gaining insight into the 'driving forces' of chemical reactions. Two of these concepts will now be considered.

Standard Enthalpies of Formation

The basic generalization:

$$\text{Enthalpy change} = \Sigma H_{(products)} - \Sigma H_{(reactants)}$$

indicates that if the enthalpies (H) of all the substances involved in the reaction are known, the enthalpy change for any reaction can be calculated. However, chemists cannot at this stage, determine experimentally or theoretically the absolute value of the enthalpy of any substance. It is possible to assign to each substance an enthalpy value relative to an arbitrary standard. This is done by defining the standard enthalpy of formation as follows:

The Standard Enthalpy of Formation (ΔH_f°) of a substance is the enthalpy change that occurs when one mole of the substance is formed from its constituent elements in their standard states.

The corollary of this definition states that:

The enthalpies of all elements in their standard states are arbitrarily taken to be zero.

$$\Sigma H_{(elements)} = 0$$

The standard state of a substance is its state at atmospheric pressure and the specified temperature, usually 25°C. If an element can exist in two allotropic forms under these conditions, the normal or more stable state is accepted as the standard state, e.g. graphite and rhombic sulphur are accepted as the standard states of carbon and sulphur.

It is obviously not true that all elements or any element has zero enthalpy under these conditions. However, since it is the difference of enthalpies that matters in any enthalpy problem, the absolute value of the enthalpy is not important. Likewise, the assumption that the elements in their standard states have equal enthalpies, is not true. This assumption or convention does not affect the basis for calculating enthalpy changes, because in physical and chemical changes, no element is changed into another.

Accepting this convention of zero enthalpy for elements, it can be seen that for the formation of a compound:

$$\text{constituent elements} \longrightarrow \text{compound}$$

The relationship $\Delta H^\circ = H_{(compound)} - \Sigma H_{(constituent\ elements)}$,

becomes $\Delta H^\circ = H_{(compound)}$, because $\Sigma H_{(elements)} = 0$

Thus, the standard enthalpy of formation (ΔH°_s) can be substituted for the absolute enthalpy (H) of the compound, so that the basic relationship for any reaction or physical change becomes:

$$\Delta H^\circ = \Delta H^\circ_{f(products)} - \Sigma\Delta H^\circ_{f(reactants)}$$

Determination of Standard Enthalpies of Formation

Standard enthalpies of formation have been obtained by two methods:

- direct experimental determination;
- derivation from other enthalpy changes, making use of the Law of Constant Heat Summation.

Examples of experimental determination:

(a) Burning of carbon in the bomb calorimeter gives the heat of combustion of carbon as 393.8 kJ mol^{-1},

i.e. $C_{(graphite)} + O_{2(g)} = CO_{2(g)} \quad \Delta H^\circ_{298} = -393.8 \text{ kJ mol}^{-1}$

(b) The enthalpy change for the union of one mole of hydrogen with one mole of iodine has been found experimentally to be 52 kJ mole^{-1}.

i.e. $H_{2(g)} + I_{2(s)} = 2HI_{(g)} \qquad \Delta H^\circ_{298} = 52 \text{ kJ mol}^{-1}$

The standard enthalpy of formation of hydrogen iodide is 26 kJ since two mole of HI are formed.

Calculation of Standard Enthalpies of Formation

In many cases heats of combustion provide the necessary data for the calculations.

Example

To determine the standard heat of formation of methane from the following data:

$$CH_{4(g)} + 2O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H^\circ_{298} = -890.4\ kJ \ldots\ldots\ldots (i)$$

$$C + O_{2(g)} = CO_{2(g)} \quad \Delta H^\circ_{298} = -394\ kJ \ldots\ldots\ldots (ii)$$

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} = H_2O_{(l)} \quad \Delta H^\circ_{298} = -286\ kJ \ldots\ldots\ldots (iii)$$

To prepare methane (CH_4) from $C_{(graphite)}$ and H_2, equation (ii) is added to twice equation (iii). And since CH_4 is required as the product, equation (i) is reversed.

(ii) $C_{(graphite)} + O_2 = CO_2 \quad \Delta H^\circ_{298} = -394 kJ$

twice (iii) $2H_2 + O_2 = 2H_2O \quad \Delta H^\circ_{298} = -572\ kJ$

reverse (i) $CO_2 + 2H_2O = CH_4 + 2O_2 \quad \Delta H^\circ_{298} = +890\ kJ$

Adding $C_{(graphite)} + O_{2(g)} + 2H_{2(g)} + O_{2(g)} + CO_{2(g)} + 2H_2O_{(l)} = CO_{2(g)} + 2H_2O_{(l)} + CH_{4(g)} + 2O_{2(g)}$

i.e. $C_{(graphite)} + 2H_{2(g)} = CH_{4(g)}$

Heat of formation of methane, ΔH°_f

$$= (-394\ kJ) + (-572\ kJ) + (+890\ kJ)$$
$$= -76\ kJ\ mol^{-1}$$

Alternatively,

heat of combustion of methane = (sum of heats of formation of the products) − (sum of heats of formation of the reactants).

$$\Delta H^\circ_{comb}(CH_4) = \Sigma \Delta H^\circ_{f(products)} - \Sigma \Delta H^\circ_{f(reactants)}$$
$$= [\Delta H^\circ{}_f(CO_2) + 2.\Delta H^\circ_f(H_2O)] - [\Delta H^\circ_f(CH_4) + 2\Delta H^\circ_f(O_2)]$$
$$= \Delta H^\circ_f(CO_2) + 2.\Delta H^\circ_f(H_2O) - \Delta H^\circ_f(CH_4)$$

(Since $\Delta H^\circ_f(O_2) = O$)

$$\therefore \quad \Delta H^\circ_f(CH_4) = \Delta H^\circ_f(CO_2) + 2.\Delta H^\circ_f(H_2O) - \Delta H^\circ_{comb}(CH_4)$$
$$= (-394\ kJ) + 2(-286\ kJ) - (-890\ kJ)$$
$$= (-394 - 572 + 890)\ kJ$$
$$= -76\ kJ$$

Example

Determine the standard heat of formation of methanol from the following data:

$$CH_3OH_{(l)} + \tfrac{3}{2}O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H^\circ_{298} = -726\ \text{kJ}$$

$$C_{(graphite)} + O_{2(g)} = CO_{2(g)} \qquad \Delta H^\circ_{298} = -394\ \text{kJ}$$

$$H_{2(g)} + \tfrac{1}{2}{}_{(g)} = H_2O_{(l)} \qquad \Delta H^\circ_{298} = -286\ \text{kJ}$$

$$\begin{aligned}
\Delta H_{comb}\,(CH_3OH) &= \Sigma\Delta H^\circ_{f(products)} - \Sigma\Delta H^\circ_{f(Reactants)} \\
&= \Delta H^\circ_f(CO_2) + 2\Delta H^\circ_f(H_2O) \\
&\qquad - \Delta H^\circ_f(CH_3OH) - \tfrac{3}{2}\Delta H^\circ_f(O_2) \\
\therefore\ \Delta H^\circ_f(CH_3OH) &= \Delta H^\circ_f(CO_2) + 2\Delta H^\circ_f(H_2O) \\
&\qquad - \Delta H^\circ_{comb}(CH_3OH) - O \\
&= -394\ \text{kJ} + 2(-286\ \text{kJ}) - (-726\ \text{kJ}) \\
&= (-394 - 572 + 726)\ \text{kJ} \\
&= (-966 + 726)\ \text{kJ} \\
&= -240\ \text{kJ}
\end{aligned}$$

The standard heat of formation of methanol is -240 kJ.

Using methods similar to those above, the standard heats of formation of many compounds have been derived. Table 5 shows some examples selected from chemical data books.

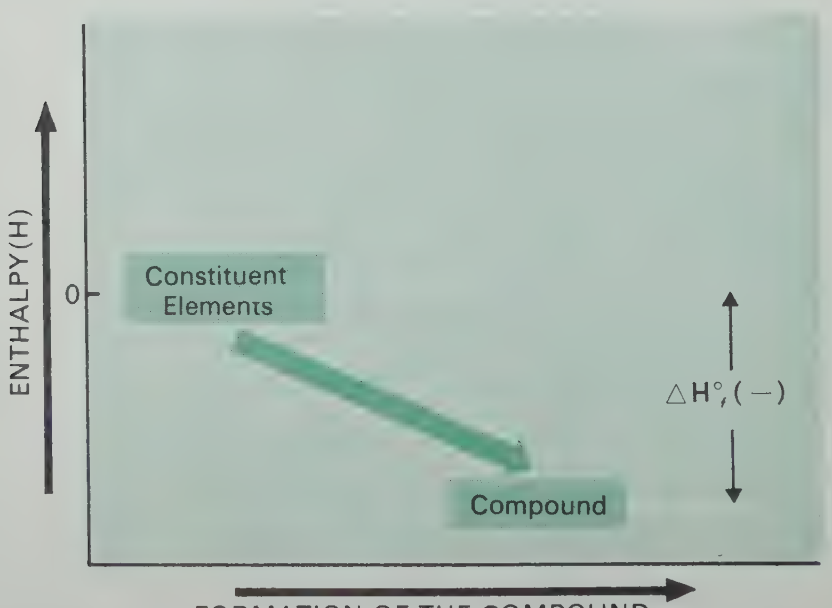


Figure 15. Standard enthalpy of formation of an exoergic compound

Table 5. Standard enthalpies of formation ($\Delta H^\circ_{(f)}$ *in kJ* mol^{-1})

	kJmol		kJmol
$Al_{(s)}$	0	$H_2O_{2(l)}$	−192
$Al_2O_{3(s)}$	−1670	$H_2S_{(g)}$	−20
$Al_2(SO_4)_3$	−3435	$HgS_{(s)}$	−58
$CaC_{2(s)}$	−62.8	$HgO_{(s)}$	−91
$CaO_{(s)}$	−635.6	$HNO_{3(l)}$	−173
$Ca(OH)_{2(s)}$	−986.6	$NH_{3(g)}$	−46
$C_2H_{2(g)}$	+227	$N_2H_{(l)}$	+50
$C_2H_{4(g)}$	+52	$NH_4Cl_{(s)}$	−315
$CH_{4(g)}$	−76	$Ni(CO)_{4(g)}$	−605
$C_6H_{6(l)}$	+49.0	$NO_{(g)}$	+90.4
CH_3OH	−240	$NO_{2(g)}$	+34
$CO_{(g)}$	−110	$O_{2(g)}$	0
$Cr_{(s)}$	0	$O_{3(g)}$	+142
$Cr_2O_{3(s)}$	−1128	$P_{(s)}$ white	0
$CuO_{(s)}$	−155	$P_{(s)}$ red	−18
$Fe_2O_{3(s)}$	−822	$P_{4(g)}$	−55
$H_{2(g)}$	0	$AgCl_{(s)}$	−127
$HI_{(g)}$	+26	$SiO_{2(s)}$	−859
$H_2O_{(l)}$	−286	$SO_{2(g)}$	−297
$H_2O_{(g)}$	−242	$TiO_{2(s)}$	−912

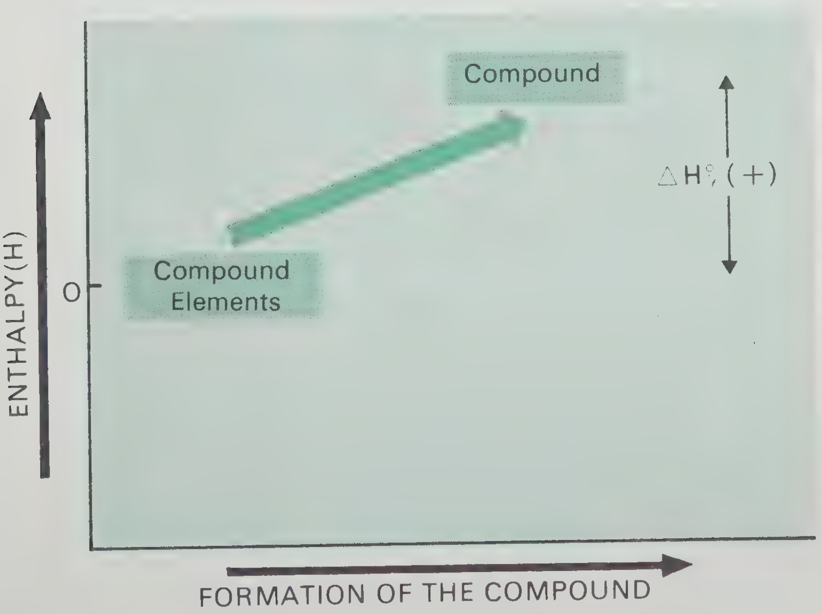


Figure 16. Standard enthalpy of formation of an endoergic compound

It will be noted that for most of these compounds the ΔH° values are negative. This implies that the compound has less enthalpy than the constituent elements and energy is given out during its formation from these elements.

In those cases where the ΔH° value is positive, energy is absorbed during its formation from the elements and the compound has a greater enthalpy than the total enthalpy of its constituent elements.

Using the Standard Enthalpies of Formation

Once a table of standard enthalpies of formation has been obtained, it is possible to use the values listed to predict the enthalpy change for any reaction, by substituting in the formula:

$$\Delta H^\circ = \Sigma \Delta H^\circ(\text{products}) - \Sigma \Delta H^\circ(\text{reactants})$$

Example

Obtain the enthalpy change for the polymerization of acetylene to form benzene.

$$3C_2H_{2(g)} = C_6H_{6(l)}$$

$$\begin{aligned}\Delta H^\circ_{298} &= \Sigma \Delta H^\circ_{f\,(products)} - \Sigma \Delta H^\circ_{(Reactants)} \\ &= \Delta H^\circ_{f\,(benzene)} - 3\Delta H^\circ_{f\,(acetylene)} \\ &= +49.0\text{ kJ} - 3 \times (+227\text{ kJ}) \\ &= (49.0 - 681)\text{ kJ} \\ &= -632\text{ kJ}\end{aligned}$$

This polymerization is strongly exoergic.

Example

To obtain the enthalpy change for the formation of ammonium chloride from ammonia and hydrogen chloride gas:

$$NH_{3(g)} + HCl_{(g)} = NH_4Cl_{(s)}$$

$$\begin{aligned}\Delta H^\circ_{298} &= \Delta H^\circ_f(NH_4Cl) - \Delta H^\circ_f(NH_3) - \Delta H^\circ_f(HCl) \\ &= -315\text{ kJ} - (-46\text{ kJ}) - (-92.5\text{ kJ}) \\ &= -176.5\text{ kJ} \\ &= -177\text{ kJ}\end{aligned}$$

Summary

Standard enthalpies of formation provide:

- a systematic and reasonably concise method of storing thermochemical data;
- a basis for calculating the enthalpy changes for all reactions where the relevant enthalpies of formation are known.

Exercises

In each of the following questions it will be necessary to consult table 5 to obtain the required enthalpies of formation.

38 The Thermite process in which powdered aluminium reacts with iron oxide is sometimes used for welding iron because the iron produced is in the molten state.

$$2Al_{(s)} + Fe_2O_{3(s)} \longrightarrow 2Fe_{(s)} + Al_2O_{3(s)}$$

Calculate the heat produced in the above reaction

[Ans: —848 kJ]

39 One stage in the purification of nickel is conversion of the nickel to the gas nickel carbonyl ($Ni(CO)_4$), according to the equation:

$$Ni_{(s)} + 4CO_{(g)} \longrightarrow Ni(CO)_{4(g)}$$

Calculate the enthalpy change for this reaction. [Ans: —163 kJ]

40 A mixture of concentrated nitric acid and hydrazine has been tested as a possible fuel for rockets; the exothermic reaction is indicated by the following equation:

$$4HNO_{3(l)} + 5N_2H_{4(l)} \longrightarrow 7N_{2(g)} + 12H_2O_{(g)}$$

Calculate the energy released by this reaction. [Ans: —2462 kJ]

41 Most of the methanol used today is prepared synthetically, by causing a mixture of carbon monoxide and hydrogen to combine when passed over a catalyst:

$$CO_{(g)} + 2H_{(g)} \longrightarrow CH_3OH_{(l)}$$

Calculate the enthalpy change for the reaction. [Ans: —128.1 kJ]

42 Calcium carbide is made by heating calcium oxide and coke in an electric furnace:

$$CaO_{(s)} + 3C_{(s)} \longrightarrow CaC_{2(s)} + CO_{(g)}$$

How much energy must be supplied to produce one mole of calcium carbide? [Ans: —462.8 kJ]

Bond Energies

In a covalent molecule of an element or compound the atoms are held together by attractive forces—electrostatic forces of attraction between the nuclei and the shared electrons. To separate the atoms work must be done against these forces, i.e. energy must be supplied. The energy necessary to separate the two bonded atoms is called the **bond energy.**

The bond energy is defined as the energy required to break the bonds when both the original substance and the products are in the gaseous state under standard conditions. The products must be separated to a distance at which the attraction is negligible.

The unit of bond energy is kJ mol^{-1}.

Example

The bond energy of the covalent bond in the iodine molecule (I-I) is 151 kJ mol^{-1}. This means that to convert one mole of iodine molecules in the gaseous state to separate atoms in the gaseous state requires 151 kJ.

i.e. $I_{2(g)} \longrightarrow 2I_{(g)}$ $\Delta H = +151$ kJ

Determination of Bond Energies

(a) **Diatomic molecules:** If the compound (e.g. HF, HCl, HBr, HI) or element (e.g. H_2, O_2, N_2, Cl_2, F_2) is gaseous, the bond energy is equal to the atomization (dissociation) energy.

If the substance is solid or liquid, then the energy required to convert the substance to a vapour must be taken into account.

For solids:

Bond energy = heat of atomization – heat of sublimation

For liquids:

Bond energy = heat of atomization – heat of vaporization

This is illustrated by the example of bromine with $\Delta H^\circ_v = 30.6$ kJ and $\Delta H^\circ_{at} = 224$ kJ.

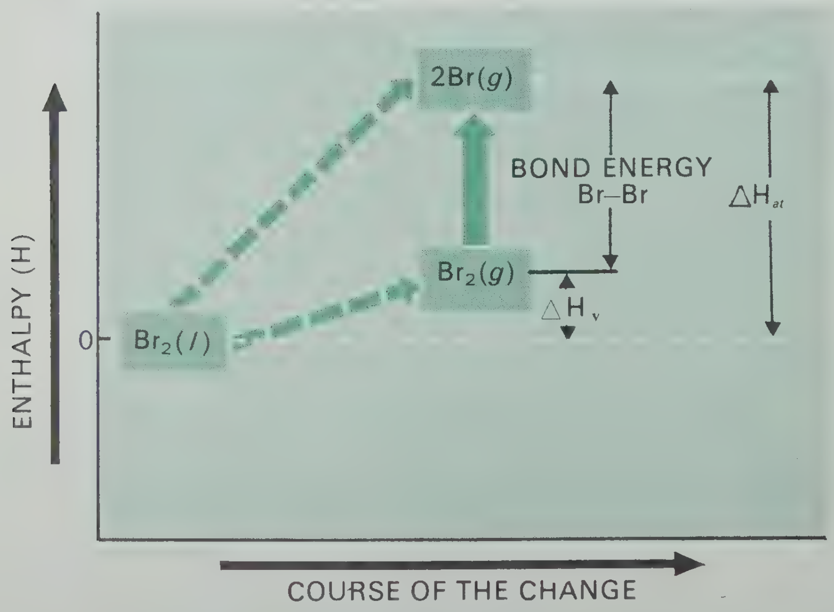


Figure 17. Illustration of the relationship (Br—Br)

$$\begin{aligned}\text{Bond energy of Br–Br} &= \Delta H^\circ_{at} - \Delta H^\circ_{v}\\ &= (224\ \text{kJ}) - (30.6\ \text{kJ})\\ &= +\,193\ \text{kJ.}\end{aligned}$$

(b) **Substances with polyatomic molecules:** For such substances, a particular bond energy may sometimes be calculated from the standard heat of formation of the compound and the dissociation energies of the constituent elements.

PROBLEM

Find the bond energy of the C—H bond in methane, given the following data:

$$\begin{aligned}\Delta H^\circ_f(CH_4) &= 76\ \text{kJ i.e. } C_{(graphite)} + 2H_{2(g)} = CH_{4(g)} & \Delta H^\circ_{298} &= -76\ \text{kJ} & \text{(i)}\\ \Delta H_{at}\,(C) &= 718\ \text{kJ i.e. } C_{(graphite)} = C_{(g)} & \Delta H^\circ_{298} &= +718\ \text{kJ} & \text{(ii)}\\ \Delta H_{at}\,(H_2) &= 436.0\ \text{kJ i.e. } H_{2(g)} = 2H_{(g)} & \Delta H^\circ_{298} &= +436\ \text{kJ} & \text{(iii)}\end{aligned}$$

Solution

The enthalpy change for the required reaction:

$$CH_{4(g)} = C_{(g)} + 4H_{(g)}$$

is obtained by adding equation (ii) to twice equation (iii), and the reverse of equation (i).

$$\begin{array}{lll}C_{(graphite)} = C_{(g)} & \Delta H^\circ_{298} = & 718\ \text{kJ}\\ 2H_{2(g)} = 4H_{(g)} & \Delta H^\circ_{298} = & 872\ \text{kJ}\\ CH_{4(g)} = C_{(graphite)} + 2H_{2(g)} & \Delta H^\circ_{298} = & 76\ \text{kJ}\\ \hline CH_{4(g)} = C_{(g)} + 4H_{(g)} & \Delta H^\circ_{298} = & 1666\ \text{kJ}\end{array}$$

This enthalpy change is the energy required to break four C—H bonds in methane. Assuming that these four bonds are equivalent we have:

$$\text{C—H bond energy} = \frac{1666}{4} = 416\ \text{kJ}$$

Using similar methods, values have been obtained for a variety of bond energies; a selection of these are set out in table 6.

Table 6. Average bond energies (kJ mol^{-1})

Bond	kJ mol^{-1}	Bond	kJ mol^{-1}
C—C	348	I—I	151
C=C	614.2	C—H	413
C≡C	839.3	C—O	358
H—H	436.0	C=O	744.8
O=O	498.3	O—H	463
N≡N	944.7	H—F	565
F—F	155	H—Cl	431.2
Cl—Cl	242	H—Br	366
Br—Br	193	H—I	299

It will be noted that all of the values listed in table 6 are positive . To break any chemical bond requires energy. Conversely, chemical bonds liberate energy.

The formation of any chemical bond is exoergic
The breaking of any chemical bond is endoergic

In chemical changes chemical bonds are broken and/or chemical bonds are formed. The net enthalpy change for the reaction is, to a first approximation, the difference between the energy required to break the bonds and the energy released by the formation of the bonds.

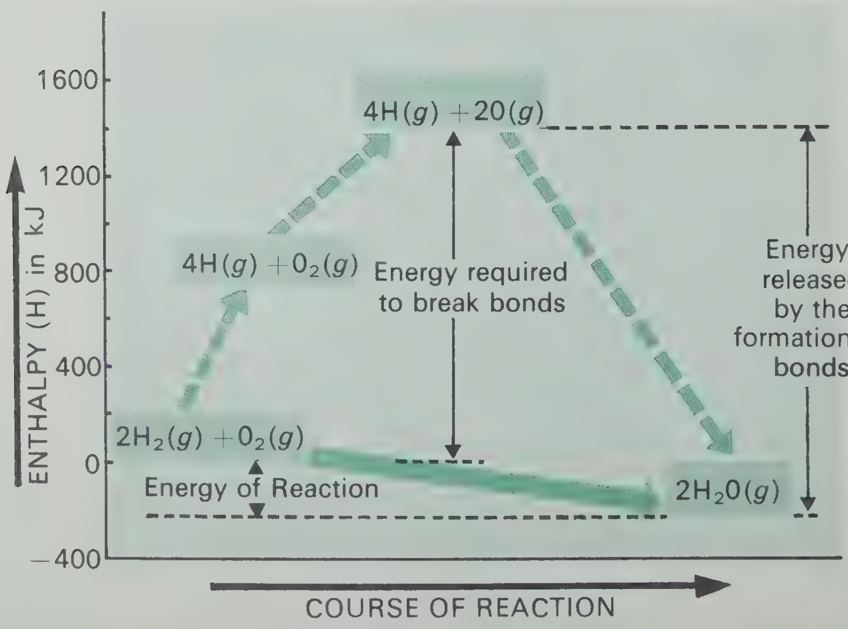


Figure 18. Enthalpy diagram to illustrate the net enthalpy change for the reaction: $2H_{2(g)} + O_{2(g)} = 2H_2O_{(g)}$

Use of Bond Energies

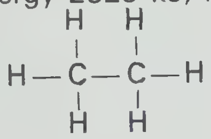
(a) Determination of other bond energies: Known bond energies can be used in the calculation of other bond energies.

PROBLEM
Find the bond energy of the C—C bond in ethane, making use of known values of the C—H bond.

Solution
Firstly the heat of atomization of ethane can be derived from the standard heat of formation of ethane and the heats of atomization of its constituent elements.

$$\begin{array}{rclcl}
\Delta H^\circ_{f(ethane)} & = & -84.5\ \text{kJ} & & \\
\therefore\ C_2H_{6(g)} & = & 2C_{(graphite)} + 3H_{2(g)} & \Delta H^\circ_{298} & = 84.5\ \text{kJ} \\
\text{also } 2C_{(graphite)} & = & 2C_{(g)} & \Delta H^\circ_{298} & = 1436.8\ \text{kJ} \\
3H_{2(g)} & = & 6H_{(g)} & \Delta H^\circ_{298} & = 1308\ \text{kJ} \\
\hline
\text{adding } C_2H_{6(g)} & = & 2C_{(g)} + 6H_{(g)} & \Delta H^\circ_{298} & = 2829.3\ \text{kJ}
\end{array}$$

This energy 2829 kJ, is the energy required to break all the bonds in ethane



$$\begin{array}{c} H\quad H \\ |\quad\ | \\ H-C-C-H \\ |\quad\ | \\ H\quad H \end{array}$$

i.e., to break six C—H bonds and one C—C bond, but the energy required to break six C—H bonds = 6 × 413 kJ

$\therefore$ the bond energy for the C—C bond = (2829—2478) kJ.
= 351 kJ.

(b) Bond energies can be used to calculate standard heats of formation.

PROBLEM
Calculate the value of $\Delta H^\circ_{(f)}$(propane).

Solution
It is necessary to find the enthalpy change for the reaction:

$$3C_{(graphite)} + 4H_{2(g)} = C_3H_{8(g)}$$

$$\text{The energy change} = \left\{\begin{array}{c}\text{energy required to} \\ \text{break bonds}\end{array}\right\} - \left\{\begin{array}{c}\text{energy released in} \\ \text{formation of bonds.}\end{array}\right\}$$

The bonds broken are those in the graphite and hydrogen molecules.

$$\begin{array}{rcl}
\text{Energy required} & = & 3 \times \Delta H_{at\,(graphite)} + 4 \times \Delta H_{at}\,(H_2)_{(graphite)} \\
& & (3 \times 718.4)\ \text{kJ} + (4 \times 436)\text{kJ} \\
& = & 2155.2\ \text{kJ} + 1744\ \text{kJ} \\
& = & 3899\ \text{kJ}
\end{array}$$

The bonds formed are the eight C—H bonds and the two C—C bonds in propane.

Energy liberated = (8 × 413) kJ + (2 × 348) kJ
= 3304 kJ + 696 kJ
= 4000 kJ

Energy change = (3899 — 4000) kJ
= —101 kJ

The standard heat of formation of propane is —101 kJ.

This type of calculation assumes that the bond energy remains constant in different molecules. This is not always true.

(c) Bond energies have been used to provide further understanding of chemical bonds.

A few examples illustrate how bond energies fit in with other approaches in the study of chemical bonds.

The bond energies of the single, double and triple bonds between carbon atoms increase progressively

C—C bond energy = 348 kJ
C=C bond energy = 614.2 kJ
C≡C bond energy = 829.3 kJ

It is found that the bond lengths, i.e. the distance between the nuclei, decrease in the same order. Both of these observations are consistent with the concept of the covalent bond. As the number of pairs of shared electrons increases, they attract the nuclei more strongly and the latter move closer together.

The bond energies can also be related to the electronegativity of the different types of atoms. The hydrides of the halogens show a progressive decrease in bond energy.

	Bond energy
HF	567 kJ
HCl	431 kJ
HBr	366 kJ
HI	299 kJ

This can be explained in terms of the decreasing electronegativity of the halogens in the order F, Cl, Br and I. This in turn can be related to the electron structure of the atom.

Exercises

43 Write thermochemical equations that correspond to the following statements:

(a) The bond energy of the H—I bond is 299 kJ mol^{-1}.

(b) The bond energy of the O = O bond is 498.3 kJ mol^{-1}.

44 Use the data in table 6 to complete the following thermochemical equations.

(a) $O_{2(g)} = 2O_{(g)} \qquad \Delta H^\circ_{298} =$

(b) $\frac{1}{2}F_{2(g)} = F_{(g)} \qquad \Delta H^\circ_{298} =$

(c) $2H_{(g)} + 2Br_{(g)} = 2HBr_{(g)} \qquad \Delta H^\circ_{298} =$

(d) $H—C \equiv C—H_{(g)} = 2H_{(g)} + 2C_{(g)} \qquad \Delta H^\circ_{298} =$

45 In the reaction $Cl_{2(g)} + H_{2(g)} = 2HCl_{(g)}$

(a) What bonds are broken during the reaction?

(b) What bonds are formed during the reaction?

(c) What is the total energy absorbed in breaking bonds?

(d) What is the total energy absorbed in forming bonds?

(e) What is the energy change for the reaction?

(f) Draw an enthalpy diagram to illustrate your answer.

[Ans: (c) 698 kJ; (d) 862 kJ; (e) —164 kJ.]

46 Use the data available in tables 4 and 6 to calculate the standard enthalpy of formation of

(a) ethylene, [Ans: 43 kJ]

(b) methyl alcohol. [Ans: —223 kJ]

Suggest an explanation of the fact that your answers differ from those listed in table 5.

47 One example of the Law of Constant Heat Summation is illustrated by the enthalpy diagram overleaf; it represents the Born-Haber Cycle for the formation of sodium chloride.

(a) From the diagram read approximate values of the enthalpy changes for:

- (i) the heat of atomization of sodium, i.e. $Na_{(s)} \longrightarrow Na_{(g)}$;
- (ii) the first ionization energy of sodium, i.e. $Na_{(g)} \longrightarrow Na_{(g)} + e^-$;
- (iii) the heat of atomization of chlorine, i.e. $\frac{1}{2}Cl_2 \longrightarrow Cl_{(g)}$;
- (iv) the electron affinity of chlorine, i.e. is, $Cl_{(g)} + e^- \longrightarrow Cl^-$;
- (v) the lattice energy of sodium chloride, i.e. $Na_{(g)} + Cl_{(g)} \longrightarrow NaCl_{(s)}$;
- (vi) the heat of formation of sodium chloride, i.e. $Na_{(s)} + Cl_{2(g)} \longrightarrow NaCl_{(s)}$

(b) Which of the above changes are endoergic and which exoergic?

(c) If we imagine that sodium chloride is formed by the five steps indicated in the diagram, which step is the major source of the energy evolved during its formation?

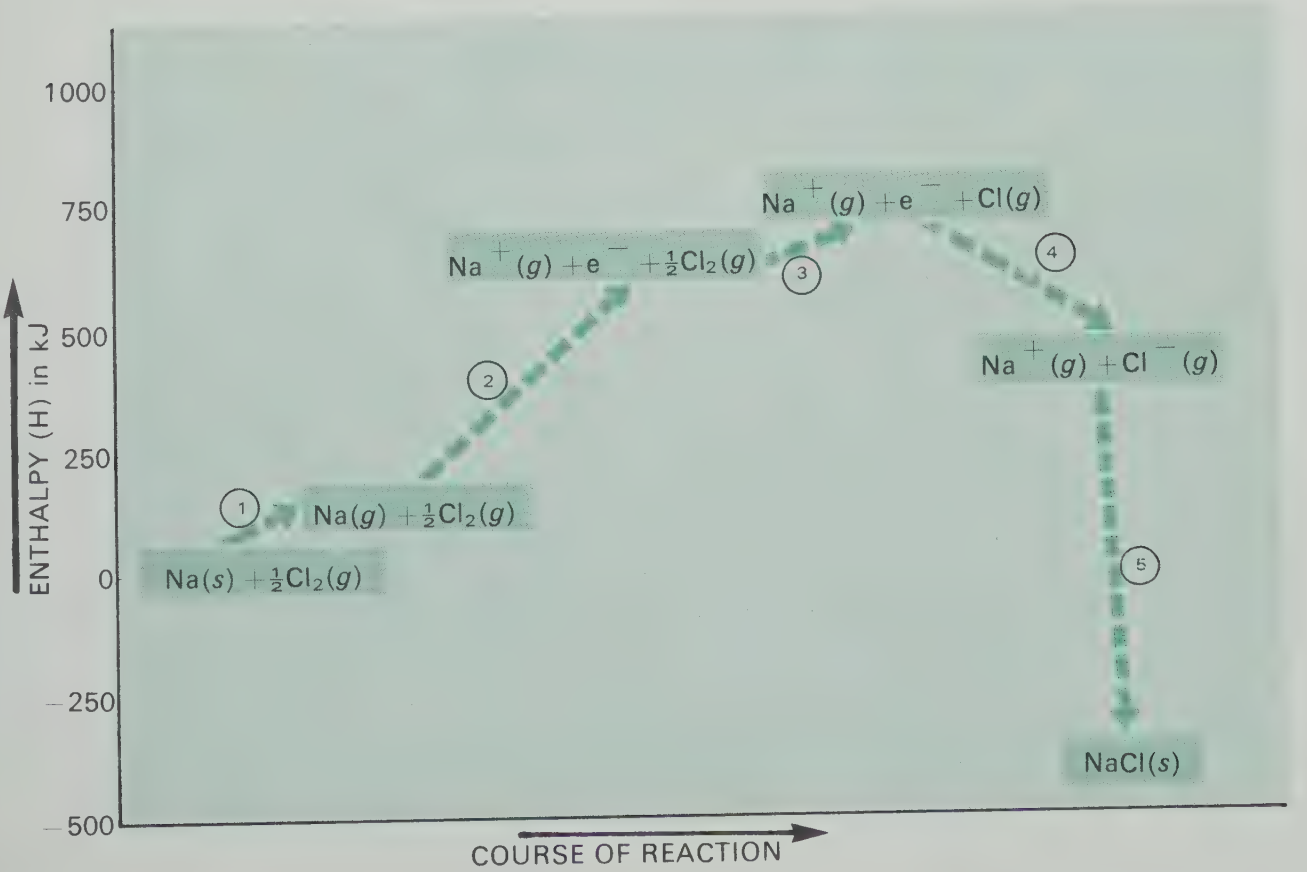


Figure 19. Born-Haber cycle for the formation of sodium chloride

Can the Direction and Extent of Chemical Changes be Predicted?

Suppose a writer of science fiction has suggested that on a certain planet—whose atmosphere does not contain oxygen—living organisms obtain the energy they need from the reaction:

$$2NH_3 + 3S = N_2 + 3H_2S.$$

Can the chemist predict—without actually trying it—whether this or any other proposed reaction is feasible? More generally, can the scientist predict whether any change—physical, chemical or nuclear—will proceed in one direction rather than another?

There are some changes of whose direction we are quite confident. We know that:

- a stretched rubber band spontaneously contracts;
- a released stone rolls downhill;
- a compressed spring spontaneously expands;
- a positively charged object moves towards a negatively charged object;
- a piece of iron spontaneously turns to rust; and
  radium automatically changes to radon and helium.

Is there any factor common to these changes? If we consider that the changes have taken place in a closed system at constant temperature, the system loses energy in each case. That is, all of these changes proceed in a direction which produces a state of lower potential energy or enthalpy.

From these and many other examples, it seems that *the tendency for potential energy or enthalpy to decrease* is *one* factor which guides the direction and extent of change.

This cannot be the only factor, because a number of changes which do not produce a decrease in potential energy or enthalpy, also occur:

- heat spontaneously moves from a hot body to a cold body in contact with it;
- a gas readily diffuses into another gas;
- ether evaporates with absorption of heat; and
- light energy is absorbed by silver chloride to form silver and chlorine.

The feature common to these changes is not so obvious. It can be shown however, that in each of these cases molecular disorder has increased.

These examples illustrate that a *second* factor which guides the direction of change is *the tendency for molecular disorder to increase*.

The degree of molecular disorder that a substance possesses is indicated by its entropy, which is represented by the letter S. Historically, entropy was introduced by the German, Rudolf Clausius, as a mathematical concept such that:

$$\Delta S = \frac{\Delta Q}{T}$$

where ΔS is the change in entropy when
ΔQ is the energy absorbed in a reversible change at the absolute temperature T.

Later, this mathematical concept was interpreted as a measure of molecular disorder since it was realized that substances with a higher entropy value had a more disordered molecular state.

Entropy increases, i.e. molecular disorder increases, when

- a solid turns to a liquid, e.g. ice melts;
- a liquid turns to a gas, e.g. methanol evaporates;
- a gas diffuses into another, e.g. the fragrance of a flower spreads through a room;
- the temperature of a substance increases;
- the number of particles increases, e.g. in the reaction:

$$CaCO_3 \quad = \quad CaO \quad + \quad CO_2$$

Consider the reaction: $NH_4Cl \quad = \quad NH_{3(g)} \quad + \quad HCl$. In this change, it can be estimated qualitatively that entropy has increased, because:

- the number of particles has increased;
- a solid has been converted to two gases.

Alternatively in the reaction:

$$3H_{2(g)} \quad + \quad N_{2(g)} \quad = \quad 2NH_{3(g)},$$

entropy has decreased because:

- four particles have formed two particles (all gases).

The tendency for entropy—or molecular disorder— to increase arises from the fact that random motion of particles is more likely to produce disorder than order. There is a greater number of possible disordered states than there are possible ordered states. If marbles are arranged in an ordered pattern on a table and then given random motion, the chance that they will end up with an ordered pattern is very small; the disorder of the marbles will tend to increase because of their random motion.

Sadi Carnot was one of the first to express what is now called the **Second Law of Thermodynamics,** but the law was given its most definite statement by Clausius in 1854, when he wrote:

'The entropy of the universe tends to a maximum'.

Free Energy

In attempting to predict the direction and extent of a possible change, two factors:

- the tendency for enthalpy to decrease;
- the tendency for entropy to increase;

must be taken into account. In some cases both factors will favour the same direction of change; if this is so, a sure prediction can be made that the change will proceed spontaneously in this direction. In other changes, the two factors oppose each other and the relative influence of each must be assessed. The influence of the tendency for entropy to increase becomes greater with rise of temperature, because the more rapid random motion increases the possibility of molecular disorder.

Mathematically, the influence of these two factors is compounded into a single concept, called **Free Energy.** This is defined by the following relationship:

free energy = enthalpy — absolute temp. × entropy

$$G = H - T \times S$$

This relationship holds under conditions of constant pressure and temperature. For any change taking place under the same conditions,

free energy change = enthalpy change — absolute temp. × entropy change

$$\Delta G = \Delta H - T\Delta S$$

Such a change will occur spontaneously only if there is a decrease in free energy, i.e. if ΔG is negative.

If ΔG is positive, the forward change will not proceed spontaneously but the reverse change will.

If ΔG is zero, a position of equilibrium has been reached and there is no tendency under the conditions considered for the change to proceed in the forward or reverse direction.

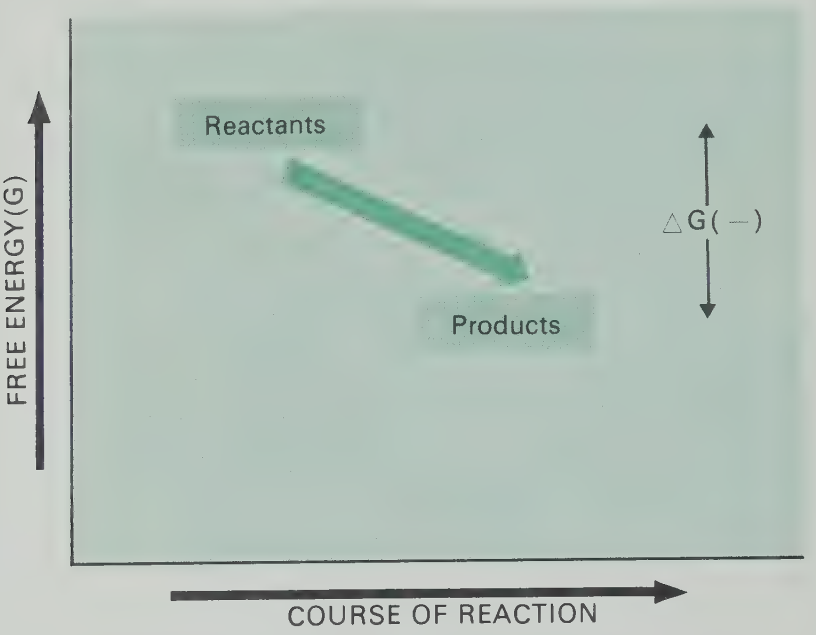


Figure 20. Free energy diagram for a spontaneous reaction

It will be seen that, if for a given change enthalpy decreases and entropy increases, both tendencies are promoting the change and it will be spontaneous. On the other hand, if enthalpy increases and entropy decreases, both tendencies favour the reverse reaction and the forward reaction will not be spontaneous. In other cases the tendencies oppose each other and a prediction cannot be made without a quantitative assessment. The summary of all four possible combinations are set out below:

Enthalpy Change ΔH	**Entropy Change S**	**Prediction**
negative (exoergic)	positive (Increased disorder)	spontaneous
positive (endoergic)	negative (Increased order)	non-spontaneous
negative (exoergic)	negative (Increased order)	may or may not be spontaneous
positive (exoergic)	positive (Increased disorder)	

For many chemical reactions, the quantitative value of ΔH can be derived from the tables of standard enthalpies of formation. In a similar way ΔS°—the change in entropy under standard conditions—can be obtained from tables of standard entropy values. From these values, the value of ΔG° at the particular temperature can be calculated. Its negative or positive value will indicate whether the change is spontaneous or not.

Nuclear Energy

Throughout his history man has relied predominantly on chemical energy—the energy arising from the attraction of the positive nuclei of atoms for the negatively charged electrons moving around them—to power his cars, his ships, his trains, aeroplanes and rockets; to warm his home and office; to mechanize the farms and factories; to produce electricity for its multiple purposes. In short, with chemical energy he has built and maintained the complex modern society. With the rapidly rising population and the increasing mechanization of society the demand for energy has become so great that the exhaustion of the fossil fuels—coal, petroleum and natural gas—has been predicted; most estimates are that they will last no more than a few hundred years. It is true that new sources of these fossil fuels are being discovered continually—Australia's recently found resources of oil and natural gas are an example—but the world's known stocks are being depleted more rapidly than they are being increased.

It is fortunate that within this century a new source of energy has become available to man, the energy arising from forces within the nuclei. The Frenchman, Henri Becquerel (1852-1908), in 1896 was the first man to obtain direct evidence of such energy. He found that uranium compounds continually emitted a form of energy that passed through light-proof paper, ionized the air, and fogged a photographic plate. This discovery of radioactivity by Becquerel initiated the study of nuclear energy; some of the results of the continued investigation over the past seventy years are only too well known. In one respect the way that nuclear energy was studied differed markedly from the development of the theory related to chemical energy. It has already been pointed out that the latter theory received its direction and stimulation from a prior practical application—the steam engine. In general, the scientific investigation of nuclear energy preceded its practical application. For about forty years it was largely an academic investigation, remote from the influence of the practical affairs of society. Becquerel carried out his experiments with uranium salts, not for any practical purpose, but to test an idea suggested by Roentgen's discovery of X-rays. The various scientists—the

Curies, Rutherford, Soddy, Einstein, Cockcroft, Walton, Chadwick, Fermi, Bethe, Hahn, Strassman, Meitner, Frisch—who developed and extended Becquerel's lead did so with much the same attitude; they were stimulated, not by the practical significance of their discoveries but rather by curiosity and the desire to extend understanding of the topic. An account of the work of these scientists is given in the NSCM Booklet S4, 'Frontiers of Science—The Atom.'

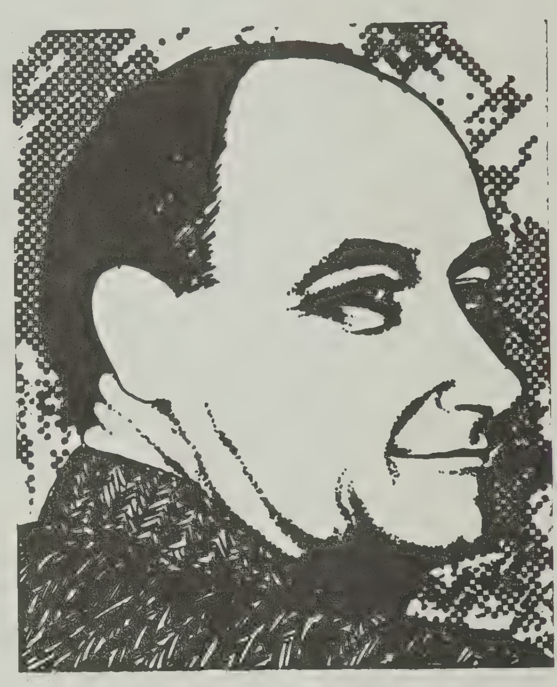


Figure 21. Enrico Fermi (1901-1954) was an Italian born physicist. The son of a minor railroad official his early interest in science was developed largely through self-study so that he became Professor of Physics at the University of Rome. Because of his work with nuclear reactions produced by the absorption of slow neutrons and the development of the first nuclear reaction, he is known as the 'father of the atomic bomb'. He was awarded the Nobel Prize and his name was given to one of the artificial elements—fermium.

Suddenly in the 1940s, the gap between the academic study of nuclear energy and the practical affairs of mankind was removed. The first nuclear reactor (1942) and the atomic bombs on Japan (1945), indicated that the results of the ideas developed in the scientists' laboratories and studies, were to have a rapid and profound effect upon society.

The work of Sadi Carnot and the study of nuclear energy represent two extremes in the interplay between science and society. Most scientists are like Sadi Carnot and are strongly influenced by the thoughts and feelings of the society in which they live; they direct their efforts to problems which are clearly related to the needs of their times.

On the other hand, some scientists—like the early investigators of nuclear reactions—select and pursue problems which are apparently far removed from the affairs of society. Frequently, it has been found that the solution of such problems has consequences for society which are as profound as the results of direct attacks on specific practical problems.

Nuclear Changes

Nuclear changes differ from physical and chemical changes in two important respects.

- In nuclear changes new elements are formed, e.g. radium may change to lead, hydrogen may change to helium.
- There is far more energy associated with nuclear changes.
- In general, nuclear changes are about 10^6 to 10^7 times more energetic than chemical changes which are, in turn, more energetic than physical changes.

The discussion on nuclear equations is dealt with more fully in the NSCM Booklet C1, A Chemist's View of the Atom, and the reader is advised to read booklet C1 in conjunction with this discussion.

Nuclear Equations

Nuclear changes can be represented by equations just as chemical changes can. In nuclear changes, the symbols must represent nuclei, not atoms or molecules. Nuclei are composed of neutrons and protons and each type of nucleus is represented by a symbol which includes numbers to indicate the composition of the nucleus. By an extension of these ideas:

- ${}_{0}^{1}n$ represents the neutron: one nucleon and no proton;
- ${}_{-1}^{0}e$ represents the electron; negligible mass and unit negative charge.

In a nuclear change the total number of nucleons and the total electric charge is conserved, i.e. remains constant; to indicate this, the total of the mass numbers and the total of the atomic numbers on one side of the equation must be equal to those on the other side of the equation.

Examples

Radioactive decay of radium:

$$^{226}_{88}\text{Ra} \qquad ^{222}_{86}\text{Rn} + ^{4}_{2}\text{He}$$

Note: $226 = 222 + 4$ $\left(\begin{matrix}\text{mass}\\\text{numbers}\end{matrix}\right)$

and $88 = 86 + 2$ $\left(\begin{matrix}\text{atomic}\\\text{numbers}\end{matrix}\right)$

Production of californium:

$$^{238}_{92}\text{U} + ^{12}_{6}\text{C} = ^{246}_{98}\text{Cf} + 4^{1}_{0}\text{n}$$

Transmutation of lithium:

$$^{7}_{3}\text{Li} + ^{1}_{1}\text{H} = ^{4}_{2}\text{He} + ^{4}_{2}\text{He}$$

Production of neutrons:

$$^{4}_{2}\text{He} + ^{9}_{4}\text{Be} = ^{12}_{6}\text{C} + ^{1}_{0}\text{n}$$

Types of Nuclear Reactions

Very many nuclear changes have been discovered and studied; these may be classified as four main types:

(a) radioactive decay;
(b) artificial transmutation;
(c) fission;
(d) fusion.

(a) **Radioactive decay** When a nucleus is unstable, it disintegrates with the emission of:

an alpha particle ($^{4}_{2}\text{He}$); or
an electron($-^{0}_{1}\text{e}$); or
a positron ($+^{0}_{1}\text{e}$); . . .

accompanied in some cases by the emission of gamma rays. Each decay is characterized by its own rate of decay which is not dependent upon temperature, pressure or any other controllable condition. This rate is described by its half-life period.

Examples

	Half-life period
Decay of carbon—14: $^{14}_{6}\text{C} = ^{13}_{6}\text{C} + ^{2}_{1}\text{H}$.	6000 years
Decay of cobalt —60: $^{60}_{27}\text{Co} = ^{60}_{28}\text{Ni} + ^{0}_{-1}\text{e}$.	5.3 years

Note: The half-line period indicates the time taken for half of the nuclei in the original sample to undergo decay.

(b) **Artificial Transmutation** In 1919 Rutherford bombarded nitrogen with alpha particles from a radioactive source, and induced transmutation to produce oxygen and hydrogen.

$$^{4}_{2}\mathrm{He} + ^{14}_{7}\mathrm{N} = ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}$$

It was later found that many nuclear changes could be produced by bombarding targets of the various elements with particles such as helium ions, hydrogen ions, deuterium ions, electrons, neutrons and protons. Generally the product was a nucleus of approximately the same atomic weight as the target. Occasionally the new nuclei were ones that did not occur naturally; some of these were radioactive.

Examples

$$^{9}_{4}\mathrm{Be} + ^{1}_{1}\mathrm{H} = ^{8}_{4}\mathrm{Be} + ^{2}_{1}\mathrm{H}$$

$$^{14}_{7}\mathrm{N} + ^{2}_{1}\mathrm{H} = ^{12}_{6}\mathrm{C} + ^{4}_{2}\mathrm{He}$$

(c) **Fission** This type of reaction was first detected when heavy nuclei such as that of uranium—235, were bombarded by neutrons. This type differed from previous types of reaction in that:

- the new nuclei produced were approximately half the atomic mass of the original heavy nucleus;
- much greater quantities of energy were produced;
- further neutrons were among the reaction products and under the right conditions these allow a chain reaction to be produced.

Examples

$$^{1}_{0}\mathrm{n} + ^{235}_{92}\mathrm{U} = ^{148}_{57}\mathrm{La} + ^{85}_{35}\mathrm{Br} + 3\,^{1}_{0}\mathrm{n}$$

$$^{1}_{0}\mathrm{n} + ^{239}_{94}\mathrm{Pu} = ^{140}_{57}\mathrm{La} + ^{97}_{37}\mathrm{Rb} + 3\,^{1}_{0}\mathrm{n}$$

(d) **Fusion** The union of light nuclei to form heavier ones, results in the release of even greater amounts of energy per unit mass than do other types of nuclear changes. It is believed that this type of nuclear change is responsible for the energy of the sun and the stars.

To bring the positively charged nuclei together requires very great energy, such as that supplied by the extremely high temperature within the centre of stars, or produced by the explosion of an atomic bomb.

Scientists are seeking methods to attain the necessary temperatures by other means so that the energy from fusion may be available for peaceful purposes.

Examples

On the sun:

$$4\,{}^{1}_{1}\mathrm{H} = {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{1}\mathrm{e}$$

Proposed fusion of heavy hydrogen:

$${}^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} = {}^{3}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H}$$

Some of the concepts which have been found helpful with regard to chemical changes can also be applied to nuclear changes.

Exoergic and Endoergic Nuclear Changes

In representing the energy changes associated with nuclear changes, different conventions from those for thermochemical equations are employed.

- The unit of energy used is the electron volt (eV); equivalent to 1.60×10^{-19} joule. A more practical unit is the million electron volt (MeV) which is equivalent to 1.60×10^{-13} kJ.

$$1 \text{ MeV} = 1.60 \times 10^{-13} \text{ kJ}$$

- The energy is not represented as a ΔH value, but is included in the actual equation.

Energy emitted is represented as a positive quantity; energy absorbed as a negative quantity.
The energy recorded is the energy per nucleon NOT energy per mole.

$$\begin{aligned} 1 \text{ MeV} &= 1.60 \times 10^{-13}\text{kJ} \\ &= (1.6 \times 10^{-13}\text{ kJ}) \times (6.0 \times 10^{23}\text{ mol}^{-1}) \\ &= 9.6 \times 10^{10}\text{kJ mol}^{-1} \end{aligned}$$

Example
The radioactive decay of radium has the following step:

$$^{226}_{88}\text{Ra} = ^{222}_{86}\text{Rn} + ^{4}_{2}\text{He} + 4.88 \text{ MeV}$$

$$\begin{aligned} \text{Since } 1 \text{ MeV} &= 9.6 \times 10^{10}\text{kJ mol}^{-1} \\ 4.88 \text{ MeV} &= 4.68 \times 10^{11}\text{kJ mol}^{-1} \end{aligned}$$

i.e. 226 g of radium releases 4.68×10^{11} kJ in this radioactive decay step.

The comparison of the energy released in a chemical reaction to the energy released in a nuclear reaction is discussed in the NSCM booklet C1. A Chemist's View of the Atom

Most nuclear reactions are exoergic, e.g.:
Radioactive decay of radium:

$$^{226}_{88}\text{Ra} = ^{222}_{86}\text{Rn} + ^{4}_{2}\text{He} + 4.88 \text{ MeV.}$$

Artificial production of magnesium:

$$^{23}_{11}\text{Na} + ^{4}_{2}\text{He} = ^{26}_{12}\text{Mg} + ^{1}_{1}\text{H} + 1.81 \text{ MeV.}$$

Fission of uranium—235:

$$^{1}_{0}\text{n} + ^{235}_{92}\text{U} = ^{141}_{56}\text{Ba} + ^{92}_{36}\text{Kr} + 3^{1}_{0}\text{n} + 200 \text{ MeV.}$$

Fusion:

$$4^{1}_{1}\text{H} = ^{4}_{2}\text{He} + 2^{0}_{1}\text{e} + 26.7 \text{ MeV.}$$

Some examples of endoergic nuclear reactions include:
Rutherford's first artificial transmutation:

$$^{14}_{7}\text{H} + ^{4}_{2}\text{He} = ^{17}_{8}\text{O} + ^{1}_{1}\text{H} - 1.16 \text{ MeV.}$$

The conversion of silicon to an isotope of phosphorus.

$$^{28}_{14}\mathrm{Si} + ^{4}_{2}\mathrm{He} = ^{31}_{15}\mathrm{P} + ^{1}_{1}\mathrm{H} \; -2.23 \text{ MeV.}$$

Nuclear Reactions and the Second Law of Thermodynamics

The Second Law of Thermodynamics is considered a universal law of nature and we can expect that it would be as applicable to nuclear changes as to chemical and physical changes. Yet most textbooks devoted to the study of nuclear changes make no reference to it; the word entropy does not appear in the index. The explanation of this is that in nuclear changes the enthalpy factor is so large that it overwhelms the entropy factor to such an extent that the latter can be ignored even at the very high temperature present in the stars. In other words, in the equation:

$$\Delta G = \Delta H - T\Delta S$$

ΔH is so large compared with ΔS, that at most temperatures $\Delta G \approx \Delta H$.

It is for this same reason that other chemical concepts such as reversibility and equilibrium have little application in nuclear reaction.

Nevertheless, it is reasonable to expect that at exceedingly high temperatures the quantity $T\Delta S$ would equal and then exceed ΔH and these concepts would then become relevant. One author has calculated that at a temperature of approximately 10^{10}K the helium nucleus would decompose into hydrogen nuclei.

$$\text{i.e. } ^{4}_{2}\mathrm{He} = + \; 4\,^{1}_{1}\mathrm{H}$$

Activation Energy and Catalysis

As with chemical changes, activation energy must be supplied before some nuclear changes will proceed. Activation energy is particularly high when two positively charged nuclei must be brought together to promote the reaction. The greater the charges on the nuclei, the greater the repulsive force that must be overcome. This explains the need for the high energy devices—the cyclotrons, the synchrotrons, the linear accelerators, etc.—which are used to give particles the energy necessary to approach and penetrate the target nuclei. Another method for providing the required activation energy, is to raise the material to a high temperature. It is estimated that to produce fusion of deuterium

$$ {}^{2}_{1}H + {}^{2}_{1}H = {}^{3}_{2}He + {}^{1}_{0}n $$

requires a temperature of more than 100 million degrees Celsius. It is the production and maintenance of such high temperatures that is one of the problems facing scientists who are seeking to attain the controlled release of thermonuclear energy.

The concept of catalysis is also relevant to nuclear change. This can be illustrated by a process which is believed to take place within the sun and other stars—the process of fusion of hydrogen nuclei by means of the **Carbon Cycle.**

The carbon cycle consists of the following series of reactions:

$$ {}^{1}_{1}H + {}^{12}_{6}C \longrightarrow {}^{13}_{7}N $$

$$ {}^{13}_{7}N \longrightarrow {}^{13}_{6}C + {}^{0}_{1}e $$

$$ {}^{1}_{1}H + {}^{13}_{6}C \longrightarrow {}^{14}_{7}N $$

$$ {}^{1}_{1}H + {}^{14}_{7}N \longrightarrow {}^{15}_{8}O $$

$$ {}^{15}_{8}O \longrightarrow {}^{15}_{7}N + {}^{0}_{1}e $$

$$ {}^{1}_{1}H + {}^{15}_{7}N \longrightarrow {}^{12}_{6}C + {}^{4}_{2}He $$

$$ \text{Net reaction: } 4\,{}^{1}_{1}H = {}^{4}_{2}He + 2\,{}^{0}_{1}e + 26.7\text{ MeV.} $$

In this reaction the carbon nucleus ${}^{12}_{6}C$, acts as a catalyst, as it allows the fusion of hydrogen nuclei to take place at a lower temperature and is itself unchanged.

In summary, most of the concepts applied to chemical energetics are applicable to nuclear changes, but because of the very great energy changes involved, some of these—entropy, reversibility, equilibrium—are not relevant except at exceedingly high temperatures.

The Social Impact of Nuclear Energy

Nuclear energy has already had a direct and significant influence on human affairs:

- it destroyed hundreds of thousands of lives at Hiroshima and Nagasaki in 1945.
- the energy from radioisotopes has been used for many beneficial purposes, e.g.
    - the gamma rays from cobalt-60 are used to destroy cancerous growths;
    - radioactive iodine-131 is used in the diagnosis of abnormal activity of the thyroid gland;
    - gamma rays are used to increase the natural genetic mutation rate and thus produce valuable new strains of plants and animals;
    - radiographs are employed in industry to detect internal flaws in welds and metal components of machines;
    - insects and bacteria are destroyed by irradiating materials such as grain and meat, with gamma rays from radioactive elements.
- the energy from nuclear reactors provides power for ocean transport—both surface ships and submarines—and for the production of electricity in an increasing number of countries.

However, the greatest impact of nuclear energy has been on the fears and hopes of mankind.

The fears of mankind are for:

- the prospect of a nuclear war which could destroy civilization and a large proportion of mankind;
- the possibility that radioactive fallout from atomic bomb tests and radiation from the waste material of nuclear reactors may directly injure present generations, and by genetic damage maim or destroy future generations.

The greatest hope is that scientists will master and control the fusion process and thereby make available to man abundant energy to supply all foreseeable needs.

Exercises

48 Could the formula

$$\Delta H = \Sigma \Delta H_f^\circ \text{ (products)} - \Sigma \Delta H_f^\circ \text{ (reactants)}$$

be applied to nuclear reactions? Give a reason for your answer.

49 Energy released during a chemical change is derived mainly from the attractive forces between opposite electrical charges. What is the main source of the energy released during nuclear changes?

50 A scientist (Peter Chapman, *'New Scientist'*, 1970) has suggested that the use of increasing quantities of energy from fossil and/or nuclear fuels may cause an increase in the temperature of the earth's surface with drastic consequences for man. He recommended greater reliance upon solar energy. Can you explain his preference for solar energy?

Reading List

Allen, J. A. *Energy Changes in Chemistry.* Allyn and Bacon, 1966. This booklet although comparatively brief is somewhat more academic than the other references and introduces some aspects that the others omit or mention briefly.

Miller, D. J. (Ed.) *Modern Chemistry and the Sixth Form.* Collins, 1965. This book contains articles by different authors on a variety of chemical topics relevant to sixth form students in England. There are two valuable articles related to chemical energetics by R. S. Nyholm & H. F. Halliwell.

Pimental, G. C. & Spratley, R. D. *Understanding Chemical Thermodynamics.* Holden-Day, 1969. Directed towards students in a general introductory chemistry course in an American University, this book discusses all the important concepts with appropriate illustrations and emphasizes the interplay between facts and theories.

Raman, V. V. 'Evolution of the Second Law of Thermodynamics' in *Journal of Chemical Education* May 1970 Vol. 47 No. 5. This article is too sophisticated for most students but for those who can understand it, the author provides a splendid historical background.

Rogers, M. (Ed.) *Energy in Chemistry* Foreground Chemistry No. 3. Heineman Education Books, 1968. This booklet was written for the Nuffield O-Level Chemistry Course and explains the fundamental ideas of thermodynamics simply and clearly.

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ENERGY IN CHEMICAL REACTIONS

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QD 501 D65 1975
Doherty, J. P.
Energy in chemical reactions.

0168449B CURR

Cover design: George Tetlow
Cover illustration: Gail

A13713

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ISBN 7715-7401-0